1969

Bench scale production of ammonium potassium polyphosphate

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BENCH SCALE PRODUCTION OF AMMONIUM POTASSIUM POLYPHOSPHATE

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

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1969

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INTRODUCTION

Trends of the Fertilizer Industry

In the past ten years the fertilizer industry has undergone a great deal of change. These changes have been in magnitude, expansion, operation, and technological improvements. Also, the fertilizer industry has been rapidly expanding throughout the world with companies increasingly conscious of the international fertilizer market (2).

In the forefront of this movement is the petroleum industry which has long been global in its operations due to the vast distances separating raw materials and markets. In the same period a major portion of the large U.S. oil companies have entered the fertilizer industry by merging with existing fertilizer manufactureres, by acquisition of mineral resources, or by building new production facilities for the primary plant nutrients. Several oil companies have already indicated that their geologists and geophysical teams will include such fertilizer minerals as phosphate ore, potassium ore, and sulfur in their global exploration for new petroleum and natural gas supplies. Fertilizer processing can be considered a logical extension of the chemical processing trend in the petroleum industry. Since the petroleum industry is internationally oriented, its influence

could be active also in overseas developments of fertilizer industries.

The trend in the chemical process industries appears to be large-scale, single stream processing units. This is due to the greater profit potential of the large scale operations. In the fertilizer industry this trend is very marked, especially in the production of synthetic ammonia, urea, sulfuric acid, and phosphoric acid. Economic factors have favored large-scale units in the United States.

Transportation is an important consideration in determining the economics of international distribution of fertilizers. The delivered cost per unit of plant food must be minimized and, the shipment of high analysis products is one method of minimizing transportation costs. As examples, special ocean going tankers have been built especially for the conveyance of liquid anhydrous ammonia and, special rubber lined tankers have been suggested for trans-oceanic shipments of phosphorus in the form of superphosphoric acid. These methods of transport substantially reduce the cost of both shipping and handling.

From 75 to 80% of the total United States ammonia production in recent years has been used for liquid or solid fertilizers. Therefore, ammonia producers consider the fertilizer market of greatest significance in their marketing. Not only has the production of ammonia increased

greatly during the past twenty years, (A long established 8 to 10% per year) but the individual plant capacity per process unit has increased spectacularly so that now units of 1000 to 1500 tons of ammonia per day are not unusual.

The trend to large-scale ammonia production has been accelerated by the use of centrifugal compressors supplanting reciprocating compressors with subsequent reductions of the unit cost of ammonia. It has been shown that the operation of a 600 ton per day ammonia plant with centrifugal compressors at only two-thirds capacity is more economical than the operation and subsequent expansion of a 400 ton per day plant with reciprocating compressors.

In addition to the production of low cost ammonia has been the trend to higher concentrations of nitrogen fertilizers such as anhydrous ammonia 82% N, urea 45% N, and ammonium nitrate 33% N. All of these products are increasingly becoming high tonnage fertilizer products in world trade due principally to their lower cost per unit of nitrogen and higher concentration (23).

The preference for potassium in the form of potassium chloride has not changed in the past thirty years. This is primarily due to the low cost and high analysis of this form of potassium. During this period the share of higher grade, more refined potassium chloride has progressively gained over the lower grades such as 41% K. The commercial large scale

production of potassium nitrate (13-0-37)[1] started in 1964. However, the proportion of potassium consumed in this form for fertilizer purposes is relatively small. Potassium chloride itself (0-0-51) is one of the most concentrated sources of plant food.

The concentration of phosphate fertilizers has tended to increase such that the once popular normal superphosphate (0-9-0) is being replaced with the increasingly favored higher analysis products such as triple superphosphate(0-20-0) and diammonium phosphate (18-20-0) in the United States and to a smaller extent in Western Europe. The higher analysis product superphosphoric acid (0-33-0) has found use in the formulation of non-precipitating liquid fertilizers and has been suggested as the form in which to transport phosphorus fertilizer for transoceanic shipments (3). With several of the major phosphate mineral reserves far removed from large consumption markets, this form of phosphorus may find a significant position in the production and global transportation of phosphate fertilizers.

The greatest growth rate of phosphate fertilizer consumption is taking place in the less developed areas such as Latin America, the Near East, the Far East, and Africa. As the main centers of fertilizer consumption tend to slowly

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[1] All analyses are given on the elemental basis as (%N-%P-%K).

move from the industrial regions to the less developed areas of the world, the growth and distribution systems of the phosphate industry will also change. With the present and planned production of world phosphate mineral deposits, many of which are far removed from commercial markets, there must be increased international transportation of phosphates. The scale of the recent and proposed phosphate production facilities lend themselves quite readily to world markets through global transportation. By combining the latest techniques, large volume and low-cost raw materials their output is produced at a lower cost per unit than in their predecessor facilities.

In addition to the increase in analysis of the single plant nutrient fertilizers, mixed fertilizers have also shown a substantial increase in plant food analysis. Since 1950 the average analysis of mixed fertilizers containing two or more primary nutrients has risen from 23.2% to 37.7% (oxide basis) in 1967 and is expected to be slightly above 43% by 1975.

Significance of the Problem

The reaction between phosphoric acid and potassium chloride to form potassium metaphosphate and hydrochloric acid has been studied on a pilot plant scale (19). The

following reactions are known to take place.

$$KCl + H_3PO_4 \triangleq KH_2PO_4 + HCl$$

$$2KH_2PO_4 \triangleq K_2H_2P_2O_7 + H_2O$$

$$K_2H_2P_2O_7 \triangleq 2KPO_3 + H_2O$$

Although the final product KPO_3 has a very high analysis (0-26-32), many problems are associated with the production of this product. Among these problems are the high temperatures required (700 → 900°C), the corrosiveness of HCl at high temperatures, and the incomplete reaction of KCl. Several methods of overcoming these difficulties have been suggested in the literature; however, these improvements have not been sufficient to promote commercial production of this product.

By increasing the H_3PO_4/KCl reactant ratio the severity of some of the above mentioned problems can be reduced. The reaction temperature is greatly reduced and the corrosion rate is much less. However, the resulting product contains a large amount of free acid (H_3PO_4). In the past it has been suggested that this excess acid be neutralized with KOH solution, which is quite expensive for a fertilizer. The product would then be dried. This process has not been used on an industrial scale since it is uneconomical.

This process could be modified by combining it with one of the present new ammonium polyphosphate processes. The final product - a complete fertilizer - could analyze approximately 10-22-17. This ratio could be modified somewhat by altering the H_3PO_4/KCl ratio in the original feed. The following unbalanced equations illustrate the products that would be expected in the above mentioned reactions.

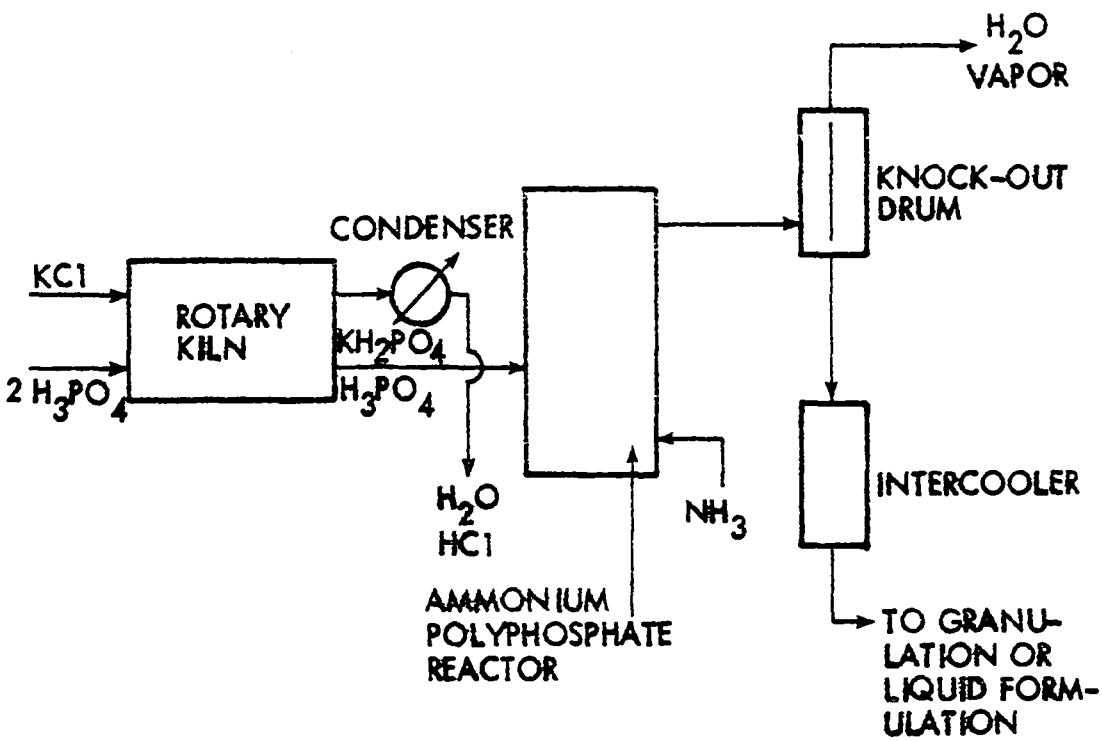
$$KCl + H_3PO_4 \text{ excess} \rightarrow KH_2PO_4 + K_2H_2P_2O_7 + HCl + H_2O + H_3PO_4$$

$$\begin{matrix} H_3PO_4 \\ KH_2PO_4 \\ K_2H_2P_2O_7 \end{matrix} + NH_3 \rightarrow \begin{matrix} NH_4KHPO_4 \\ (NH_4)_2KPO_4 \\ NH_4K_2HP_2O_7 \end{matrix} + H_2O + \text{Ammonium Polyphosphates}$$

This thesis undertakes to determine the technical feasibility of such a process. A flow diagram of the process is shown in Figure 1.

The market potential of an ammonium potassium polyphosphate fertilizer could be quite favorable for certain fertilizer uses. The product is completely water soluble and could be used as a starter fertilizer. Grades with plant food ratios of 1-2-2, 1-4-4, and 1-2.5-2 (elemental basis) could be most readily formulated. For example, 50 pounds of a 10-20-20 ammonium potassium phosphate would supply the same amount of primary nutrients as a 100 pound

Figure 1. Ammonium potassium polyphosphate flow diagram


H_2O
VAPOR
KNOCK-OUT
DRUM
CONDENSER
KCl
ROTARY
KILN
KH_2PO_4
$2\ H_3PO_4$
H_3PO_4
INTERCOOLER
H_2O
HCl
NH_3
AMMONIUM
POLYPHOSPHATE
REACTOR
TO GRANU-
LATION OR
LIQUID FORM-
ULATION

bag of 5-10-10. The low nitrogen analysis compared with phosphorus and potassium analysis in many cases is desirable since the user may prefer to apply the bulk of his nitrogen in the low cost form of anhydrous ammonia. Grade ratios such as 1:2:2 and 1:2.5:2 could be used as tobacco and potato fertilizers where low chlorine fertilizers are required. Use in liquid fertilizers could be possible if the polyphosphate content were high. It is believed that very high analysis liquid fertilizers could be formulated with ammonium potassium polyphosphates since the chloride usually associated with potassium would be absent. In many cases the concentration of liquid fertilizers is limited by the chloride content, otherwise salting-out occurs.

On the other hand, the cost of an ammonium potassium polyphosphate product would probably limit its potential for use in bulk blends when compared with granulated diammonium phosphate, triple superphosphate, and potassium chloride. Present competitive products include: potassium nitrate, ammonium polyphosphate,granulated mixed fertilizers and to some extent blends of diammonium phosphate and potassium chloride.

Several agronomic considerations are important with regard to ammonium potassium polyphosphates. The availability of all primary nutrients would be essentially one

hundred percent. The product would be expected to be completely water soluble, and perhaps impurities such as iron and aluminum may be sequestered if used in liquid fertilizers. The high water soluble phosphorus content, in association with the ammonium form of nitrogen, is most desirable in starter fertilizers. Agronomically desirable would be the homogeneity of this complete fertilizer. Reduced handling and transportation costs per unit of plant food would result due to the concentrated form of the granular ammonium potassium polyphosphate fertilizer.

The lowest cost raw material sources of nitrogen and potassium are ammonia and potassium chloride respectively. These are the same sources of nutrients for ammonium potassium polyphosphate fertilizer. Phosphoric acid, however, is an expensive form of fertilizer phosphorus.

The process heat cost required in the potassium chloride-phosphoric acid reaction portion of the proposed process would be quite high. The profit from the sale of by-product hydrochloric acid could possibly pay for a portion of this heat requirement. Chemical Construction Corporation has a commercial process for the production of potassium metaphosphate. This process could be altered using the modifications suggested in this work and integrating these modifications with present ammonium polyphosphate processes to produce ammonium potassium polyphosphate on an

industrial scale.

Specific Objectives

Theoretical and experimental objectives

Several objectives were envisioned for the proposed process.

1) To determine formulas for the products from orthophosphates to ultraphosphates of potassium and ammonia. Since chemical structures of the individual potassium phosphates and ammonium phosphates are already known, formulas for the combined ammonium potassium phosphates were to be proposed.

2) To evaluate the thermodynamics of the process, such as the heats of reaction and the heats of formation of various product constituents.

3) To determine the kinetic model of the following reaction.

$$nH_3PO_4 + KCl \rightleftharpoons KH_2PO_4 + HCl + (n-1)H_3PO_4$$

4) To determine the effect of N/P mole feed ratio, temperature, pressure, and residence time upon the degree of ammoniation of the final product.

LITERATURE REVIEW

Ammonium Potassium Phosphate

A novel method of producing a complete concentrated fertilizer (5.6-24.7-15.6) was tested on a small pilot plant scale by W. H. Ross as noted by Waggaman (31). The following main reactions were reported:

$$KCl + 2H_3PO_4 \rightarrow KH_2PO_4 + H_3PO_4 + HCl$$

$$KH_2PO_4 + H_3PO_4 + NH_3 \rightarrow KH_2PO_4 + NH_4H_2PO_4$$

The process involved two steps. In the first, potassium chloride was digested with two or more equivalent amounts of concentrated phosphoric acid at 250°C. Three products were obtained: volatilized hydrochloric acid, and a liquid solution of monopotassium phosphate and phosphoric acid. The hydrochloric acid was volatilized by aeration of the solution which consisted of blowing air, heated to approximately 200°C., through a gas distributor in the solution. The volatilized hydrochloric acid was then collected. The second step of the process consisted of diluting the monopotassium phosphate-phosphoric acid solution with an equal volume of water, ammoniating to a thick slurry of an isomorphic mixture of monoammonium and monopotassium phosphate, and drying to a nonhygroscopic fertilizer.

Potassium Phosphates

When equivalent amounts of potassium chloride and phosphoric acid are heated to produce potassium metaphosphate only a small portion of the chloride is replaced by phosphoric acid at temperatures of 200 to 300°C. However, all the chloride can be replaced and volatilized at 700 to 900°C. The resulting residue upon cooling solidifies into a hard glassy-like material.

Ross and Hazen (10,22) used an excess of phosphoric acid to completely decompose the KCl in the first step at 250°C. Any chlorides which could be carried through to the final fertilizer product were thereby removed. The reaction temperature of 250°C. for the first step was much lower than the 700° to 900°C. required for the production of potassium metaphosphate. After the volatilization of hydrochloric acid, the solution of Ross consisted of monopotassium phosphate with an equivalent amount of phosphoric acid. This solution was then diluted with water to a specific gravity of 1.50 to 1.65. Gaseous ammonia was used to neutralize the excess acid. In this manner a large proportion of the material in solution was precipitated and removed by centrifugation from the mother liquor. The precipitated solids consisted of a mixture of potassium and ammonium phosphates. It was suggested that the remaining

mother liquor could be recycled and ammoniated again. The centrifuged product was then dried to a non-hygroscopic fertilizer. Also, Ross suggested the use of a solution of ammonia for neutralizing the potassium phosphate-phosphoric acid solution. In this case the phosphate solution would have to be of a higher concentration with a specific gravity of 1.85 to 1.95 if a saturated ammonia solution were used.

In the process developed by Ross it was noted that increasing the H_3PO_4/KCl mole feed ratio from one to two decreased temperature of reaction and reduced the residence time required for the KCl to react. (No mention was made of the various residence times). However, the resulting product was diluted with water and ammonia passed into the solution until a thick slurry was obtained. This was then centrifuged and dried. Direct ammoniation as presently used in the manufacture of ammonium polyphosphate was not in use at this time (1922). Direct ammoniation of concentrated phosphoric acid was first noted in the literature in the late 1950's and early 1960's. It appears that this process could now be improved through the use of an ammonium polyphosphate reactor for the second portion of the process. This would eliminate the need for diluting the KH_2PO_4-H_3PO_4 solution and drying the resulting ammoniated product. In addition to the elimination of the dilution and drying steps, a more highly concentrated product would be formed due to the

highly exothermal reaction in the polyphosphate reactor.

When equivalent molar amounts of potassium chloride and phosphoric acid are reacted together the resultant hydrochloric acid is not completely volatilized until the potassium is completely converted to the potassium metaphosphate form. When excess potassium chloride is used normal potassium pyrophosphate is formed as shown below.

$$4KCl + 2H_3PO_4 \rightarrow K_4P_2O_7 + 4HCl + H_2O$$

Potassium metaphosphate produced at 700 to 900°C. is water insoluble. However, the phosphorus is available according to AOAC[1] official methods.

A second method of producing potassium metaphosphate was tried on a pilot plant scale at the Tennessee Valley Authority by Copson (5). This method was a modification of TVA's calcium metaphosphate manufacturing process. In this process molten potassium chloride was produced in an electric furnace and allowed to flow downward countercurrent to the flow of an upward stream of gas containing P_2O_5. This P_2O_5 was produced by burning phosphorus in moist air in a combustion chamber. The reaction between P_2O_5 and molten KCl was:

$$2KCl(l) + P_2O_5(g) \rightarrow 2KPO_3(l) + 2HCl(g)$$

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[1]American Organization of Analytical Chemists.

Many problems were encountered with this process including: solidification of potassium chloride in the upper portion of the furnace, corrosion of the tower refactory packing, and incomplete reaction of the P_2O_5 gas with the molten potassium chloride.

Potts, Elder and Scott (20) of TVA produced on a laboratory scale liquid fertilizer solutions composed of the same chemical species as found in Ross's product: concentrated phosphoric acid, ammonia and potassium without any chloride or sulfates. The low chlorine grade liquid fertilizers were made with superphosphoric acid and potassium hydroxide and ammonia. Neutral high analysis liquids could be formulated with little or no nitrogen content when made with potassium hydroxide as compared with the lower analysis acidic liquids made with potassium chloride. Some grades produced with potassium hydroxide with comparable grades made with potassium chloride are shown below:

Table 1. Fertilizer analysis using H_3PO_4, NH_3, KOH, and KCl[a]

Grade Ratio	Maximum analysis (no salting out after one week at 0°C.)	
	Using KOH	Using KCl
0:1:2	0-11-22	-[b]
2:1:2	10-5-10	8-4-8
1:1:1	9-9-9	7-7-7
1:1:2	6-6-12	4-4-8
1:1:3	5-5-15	3-3-9
1:2:2	6-12-12	3-6-6

[a]Calculated using the figures of Potts et al. (20).

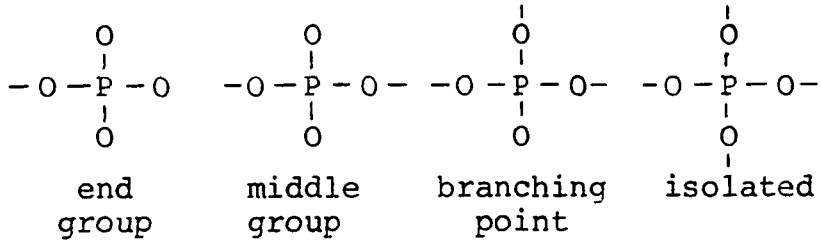
[b]Solution would be highly acidic since the phosphoric acid would not be neutralized at all.

A large amount of information is available on the molecular structure of condensed phosphates, ultraphosphates and the corresponding metal phosphates. Molecular configurations of ammonium phosphates, and condensed ammonium phosphates are also known. However the molecular structures of the ammonium-potassium combination phosphates and condensed phosphates are not known with the same degree of certainty as the previously mentioned phosphates.

Phosphate Structures

"Phosphates are defined as compounds of phosphorus in the anions of which each phosphorus is surrounded by four

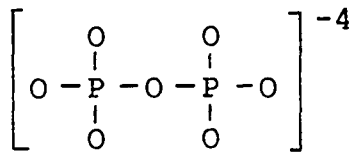
oxygen atoms arranged at the corners of a tetrahedron" (30). Three types of interconnected phosphates can be produced by the sharing of oxygen atoms between tetrahedra: chain, ring and branched polymers. Van Wazer (28) proposed that four types of structural units make up these phosphates as shown below.



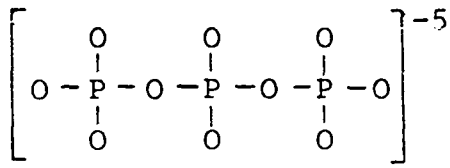
These four types of phosphate groups have been differentiated through nuclear magnetic resonance (NMR) studies of phosphate chemical bonding (29). It was found that a middle group in a chain structure was equivalent to that of a middle group in a ring structure. Also it was found that end groups had the same phosphorus oxygen bond characteristic for all chain lengths measured. Based on x-ray, pH titration, and thermodynamic data there are indications that the branching points are unstable compared with the end group and middle group (30). Structures containing cross-linking (branching points) degrade to more stable forms in aqueous solutions.

The pyrophosphate ion consists of two end groups. Straight chains consist of one or more middle groups connected to two end groups. The ring structure consists of

middle groups. The branching point can help form either branched chains or ring structures with a connected chain. The two dimensional structure of pyrophosphate can be represented as shown below:



In addition to pyrophosphoric acid many alkali metal pyrophosphates have been prepared in crystalline form. Among the more common pyrophosphate salts are those of sodium, potassium, magnesium, ammonium, and magnesium. The pyrophosphate ion is a strong complexing agent capable of sequestering charged metal ions. However, the precipitates of these multiply charged metal ions are generally quite insoluble. For the tripolyphosphate anion the following structure represents it in two dimensional form.

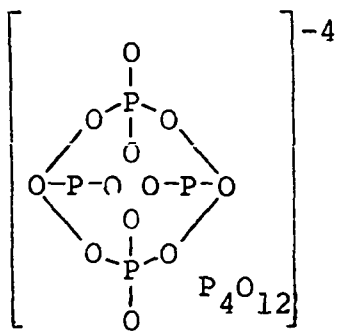


According to Dymon and King (6) the four nearest oxygen tetrahedrally surround each phosphorus atom with the P-O-P bond angles the same as the O-P-O bond angles. Proof of the existence of a linear tetrapolyphosphate has been given by Osterheld and Langguth (14).

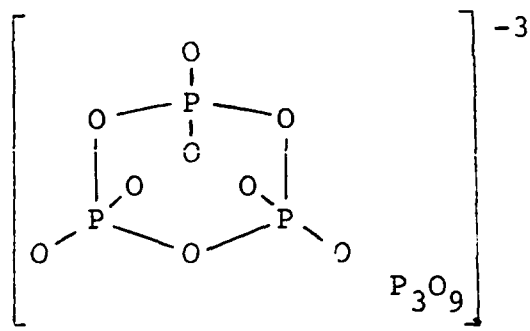
The ring phosphate compounds of multiply charged and heavy metal ions are relatively soluble in water compared with the straight chain phosphate salts. Also the ammonium, substituted ammonium salts and alkali metal salts of ring phosphates are highly soluble. The ring phosphates complexing ability is quite weak compared with that of the chain phosphates.

At a neutral pH both the ring and chain phosphates are quite stable in aqueous solutions. However, in basic solutions the ring structures rapidly split into the more stable chain structures. Also, in strongly acidic solutions the hydrolysis of the rings is catalyzed by hydrogen ions resulting in rapid break down of the ring structure.

The structures of two known ring phosphates are shown below:



Tetrametaphosphate



Trimetaphosphate

If the analogy between cyclic hydrocarbons and cyclic phosphates can be used, the six and eight membered rings should be the most readily formed and most stable. The

larger membered rings of phosphate should have a lesser probability of forming and also be less stable. Letting M represent one cation equivalent or an organic radical, the phosphates are characterized by $0 < M_2O/P_2O_5 \leq 3$. Polyphosphates are generally understood to include the range $1 < M_2O/P_2O_5 \leq 3$. The metaphosphates have a M_2O/P_2O_5 ratio of 1.0 and the ultraphosphates include the region of $0 < M_2O/P_2O_5 < 1$. The straight chain polyphosphates can be represented by the general formula $M_{n+2}\ P_nO_{3n+1}$ where n is any integer equal or greater than two. The structure of metaphosphate has the formula $(MPO_3)_n$, a ring structure, or very long chains where n approaches infinity.

Linkages such as M-O-P can be considered as ionic linkages. Thus there are two types of phosphate linkages: the M-O-P and the P-O-P. These linkages are composed of bonds or coulombic attraction between positive and negative charges. Therefore

$$N_t = (M+3P)/2$$

where N_t = total number of linkages in the phosphate structure (an integer)

P = number of phosphate atoms in the structure

M = number of cation or organic radicals in the structure

Simple phosphate structures can thus be determined using the

general ring and chain formulas, and the above linkage equation.

Superphosphoric Acid

Interest of the fertilizer industry in polyphosphoric acid is high. Polyphosphoric acid ($H_{2n}P_nO_{3n+1}$) includes pyro, tripoly, tetrapoly and higher polyphosphoric acids. Super acid contains orthophosphoric acid and at least one third of its phosphorus as polyphosphates. In the 1950's it was learned how to concentrate efficiently wet process phosphoric acid of approximately 26% P to concentrations of 30 to 35% P (18). Acids in this concentration range actually contain a mixture of various phosphoric acids ranging from orthophosphoric acid to the highly condensed polyphosphoric acids.

Two general methods are available to produce polyphosphoric acids. The most common method involves the concentration of regular 26% P wet process acid by means of a falling film evaporator or through the use of a submerged combustion technique involving the submerged burning of natural gas in phosphoric acid (7, 15). The other method is through the controlled and limited hydration of P_2O_5 from elemental phosphorus burned in air.

Polyphosphoric acids made from wet process acid usually

contain little sludge since the impurities are sequestered. It is desirable for superphosphoric acid to contain at least fifty percent of the phosphorus in the form of polyphosphates in order to adequately sequester iron and aluminum impurities or micronutrients such as zinc and manganese (26). Plants use phosphates in the form of the orthophosphates, and are known to use pyro and more highly condensed phosphates directly. The polyphosphates slowly hydrolize in the soil to the ortho form (1, 17). Phosphorus is generally recognized as the least efficiently used primary plant nutrient; usually only five to thirty percent of the applied phosphorus is utilized by the current crop. Lower efficiencies of use of the carryover are attained by subsequent crops. Orthophosphates are made unavailable to plants by reversion, such as precipitation as iron or aluminum phosphates in acid soils or calcium in basic soils. It has been proposed that polyphosphates may be more efficiently utilized by crops than the standard orthophosphates (12, 17, 27). In the soil polyphosphates convert slowly to the ortho form, thus becoming available for plant utilization over a greater period of growth. Also, the polyphosphates tend to move through the soil more than the ortho form thus increasing the probability of contact with plant roots. It should be possible to formulate phosphate fertilizers approaching a controlled release with orthophosphate for early plant use

and polyphosphates available for later use since superacid can be made with varying proportions of ortho and polyphosphoric acids.

The production of highly concentrated 30 to 35% P acids from lower concentration acid requires large heat inputs. The Tennessee Valley Authority (TVA) has found that 1.3 to 1.5 million B.T.U. per ton of phosphorus P are required to concentrate from 26% P acid to 31 to 33% P acid (24). Early work by TVA indicated that iron-aluminum tripolyphosphate solids formed during the concentration process if high retention times in the evaporator occurred. This problem was eliminated by decreasing the residence time to less than twelve minutes. Highly concentrated wet-process phosphoric acids have viscosities that vary greatly due to differences in acid purity. A 31% P acid may have a Brookfield apparent viscosity over 50,000 centipoises at room temperature and less than 2,000 centipoises at 130°C. The viscosity of concentrated phosphoric acids decrease rapidly with increasing temperature. Also, the viscosities of wet-process acids are several times as great as equally concentrated furnace acids.

The highly concentrated phosphoric acids have been used in formulating higher analysis liquid fertilizers than possible previously. Ammoniation of superphosphoric acid yields ammonium polyphosphate which is used in liquid

fertilizers or as a solid fertilizer.

Ammonium Polyphosphates

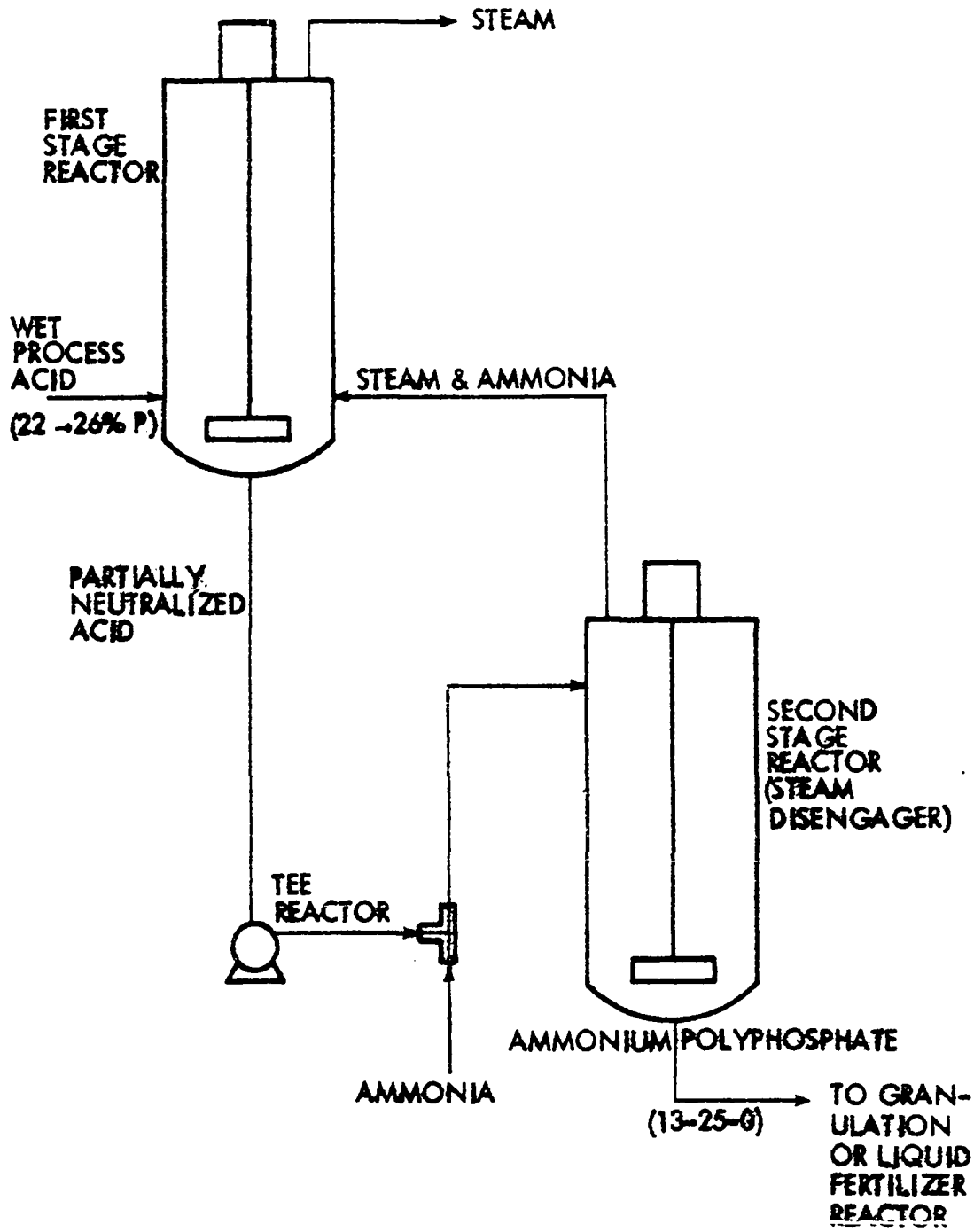
Ammonium polyphosphate analyzing approximately 13-25-0 is produced in two different ways by TVA (13). In the first and earliest method superphosphoric acid is reacted with ammonia in a pressure vessel equipped with water cooled coils. In the second method no cooling is necessary since a lower concentration phosphoric acid (24% P) is used.

The process in which super acid is used is usually operated under moderate pressure, 25 to 350 psig, and at a temperature below 232°C. Because of the heat produced by the highly exothermal reaction, cooling is required to maintain the reaction system below 232°C. According to Getsinger et al. (9) the degree of ammoniation of the product is increased by increasing the following: agitation of the reaction system, pressure, and retention time. It appears that increasing the temperature above 185°C. decreases the amount of ammoniation of the superphosphoric acid. The resulting reaction product was amorphous and plastic, and without agitation, crystallized over a period of weeks. However, when agitated the product readily crystallized while cooling. The product can be easily granulated in a pugmill with recycled fines. Product ammonium polyphosphate

consisted of crystalline material held together by an amorphous phase. Although all the crystalline material could not be identified, monoammonium orthophosphate, tetrammonium pyrophosphate, and triammonium pyrophosphate monohydrate were identified.

In the second process utilizing wet process acid of lower concentration a two stage reaction system is used. Into the first stage reactor wet process acid is fed continuously, and countercurrently anhydrous gaseous ammonia is fed into the second stage reactor (see Figure 3). Unreacted ammonia and steam generated in the second reactor are then passed into the first reactor. Heat produced by the exothermal reaction is utilized in dehydrating the solutions in each reactor and no removal of heat through heat exchangers is required. This is the major difference between the two processes since large heat inputs are required to produce super acid in the first process and subsequent cooling is required of the ammoniation reaction. From an engineering and economic viewpoint the second process is the most efficient because the heat of reaction is effectively used to produce the highly concentrated polyphosphate and the large amount of cooling required to remove the heat of reaction between superphosphoric acid and ammonia is unnecessary. The processing equipment for this second process is relatively simple in design and inexpensive to

Figure 2. TVA (11) process for direct production of ammonium polyphosphate from wet process phosphoric acid


STEAM
FIRST STAGE REACTOR
WET PROCESS ACID
(22 →26% P)
STEAM & AMMONIA
PARTIALLY NEUTRALIZED ACID
SECOND STAGE REACTOR (STEAM DISENGAGER)
TEE REACTOR
AMMONIUM POLYPHOSPHATE
AMMONIA
(13-25-0)
TO GRANULATION OR LIQUID FERTILIZER REACTOR

operate compared with that for the production and ammoniation of super acid. Product ammonium polyphosphate melt from either process can be either granulated in a pugmill to a solid product or fed directly into a liquid fertilizer reactor with water and additional ammonia to produce a 10-15-0 base liquid fertilizer solution containing over fifty percent of the phosphorus in the polyphosphate form.

Problems encountered by TVA with ammonium polyphosphate include the formation of citrate insoluble phosphates when wet process acid containing large amounts of iron and aluminum is used; and the resultant formation of insoluble solids in liquid fertilizers made from this product. The formation of citrate insoluble phosphates of iron and aluminum can usually be minimized by the proper control of pH, temperature and residence during the reaction. TVA at the present time is studying the different means for minimizing the loss of phosphorus availability.

Frazier, Smith and Lehr (8) have performed an extensive examination of the composition and properties of the constituent polyphosphates found in ammonium polyphosphates. Fourteen different compounds were isolated and chemically and physically characterized. The chemical composition of each crystalline species was determined and compared with the theoretical stoiciometric composition. These compounds included six ammonium pyrophosphates, six ammonium tripoly-

phosphates, and a long chain ammonium polyphosphate. Also, extensive information was obtained on the morphological and optical properties of the ammonium pyrophosphates. Frazier, Smith and Lehr (8) have shown that the ammoniation products of superphosphoric acid at low degrees of ammoniation (N:P mole ratio of 1.1 to 1.2) consist mostly of mixtures of NH_4HPO_4 and $(NH_4)_3HP_2O_7$; and at higher degrees of ammoniation (N:P mole ratio of 1.9 to 2.0) $(NH_4)_2HPO_4$ and $(NH_4)_4P_2O_7$. It was noted that pyrophosphates in both of the latter products behave the same in the mixtures as they do alone. The behavior of these products in storage is determined by loss of ammonia alterations and changes in hydration which are in turn influenced by the temperature and humidity.

EXPERIMENTAL INVESTIGATION

Research Plan

A general theoretical rate expression can be written for the reaction

$$nH_3PO_4 + KCl \rightleftarrows KH_2PO_4 + HCl + (n-1)H_3PO_4$$

in aqueous phase where the reverse reaction can be neglected. This expression

$$\frac{-dC_{Cl}}{d\theta} = k[C_{Cl}]^{\alpha}[C_{H_3PO_4}]^{\beta}$$

where C_{Cl} and $C_{H_3PO_4}$ = concentrations

α, β = order of reaction with respect to the component

θ = time unit

$k = k_0^{-E/RT}$ the Arrhenius equation reaction rate constant

k_0 = frequency factor

E = activation energy of the reaction

R = ideal gas law constant

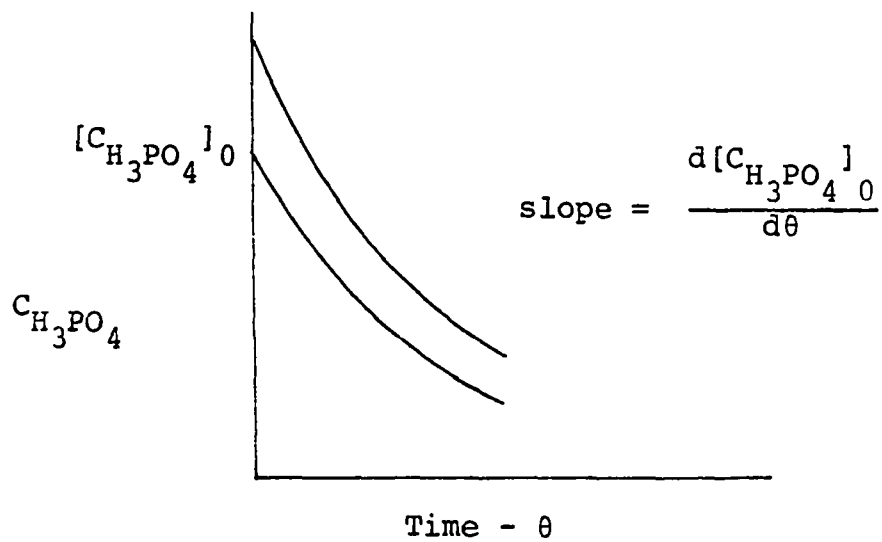
T = temperature

where potassium chloride is the limiting reactant would be desirable as a basis for the experimental determination of the frequency factor k_0, activation energy E, and the order of the reaction $\alpha\&\beta$ with respect to the reactant concentrations C_{Cl} and $C_{H_3PO_4}$. The constants α and β can be

determined in several ways. Using a heated batch reactor as shown in Figure 3 the differential method can be used to determine α and β as described below.

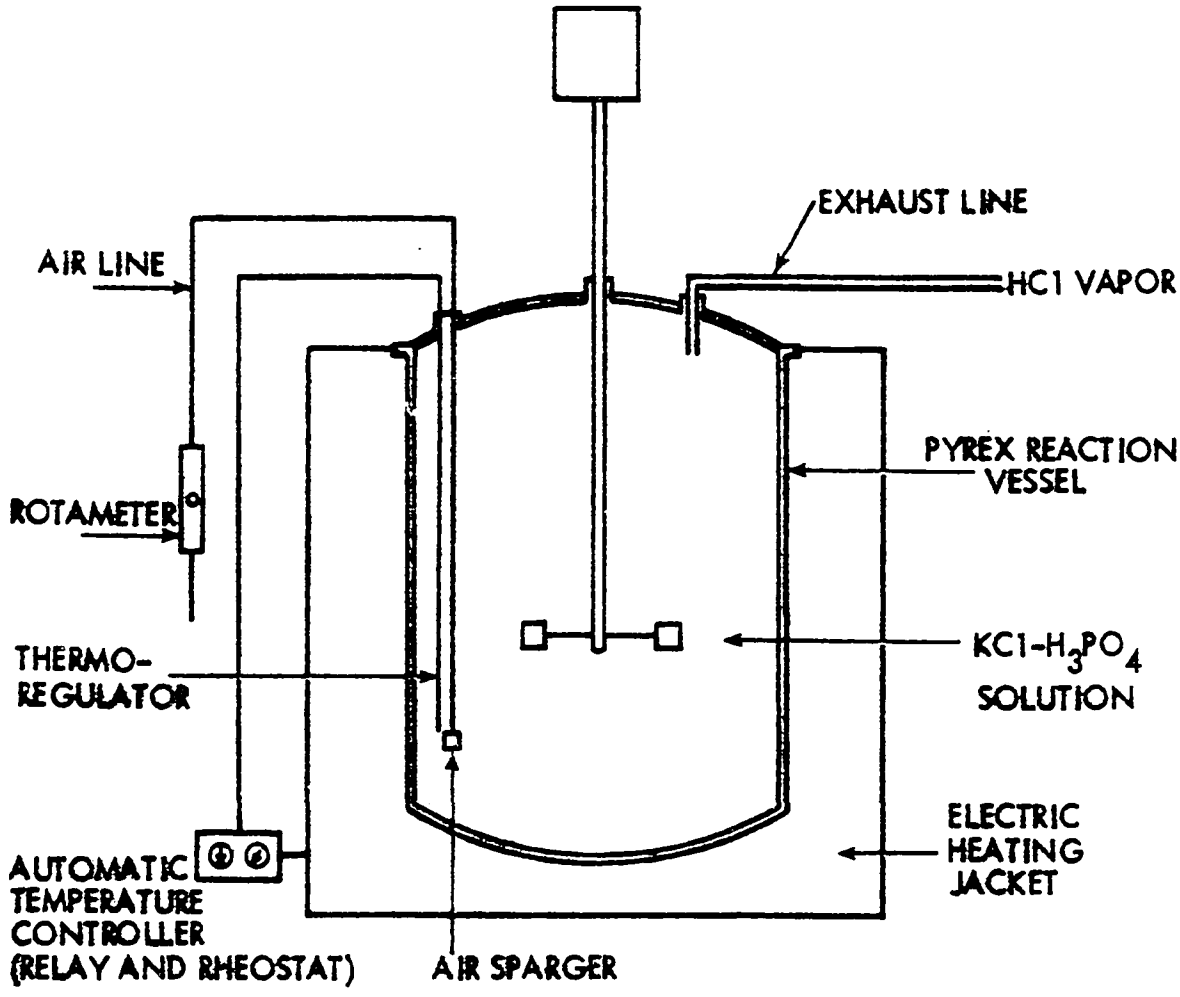
$$\log \left[\frac{-dC_{Cl}}{d\theta}\right] = \log \left(kC_{Cl}^{\alpha}\right] + \beta \log \left[C_{H_3PO_4}\right]$$

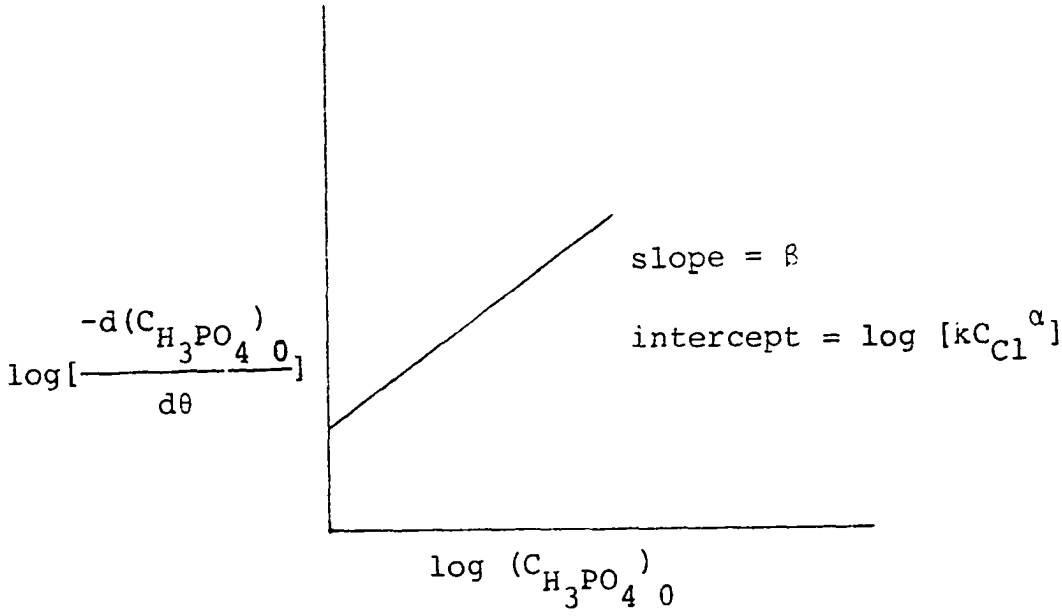
By plotting the initial concentrations of phosphoric acid versus time for a given set of experimental conditions, the rate of change of phosphoric acid concentration as a function of time can be obtained.



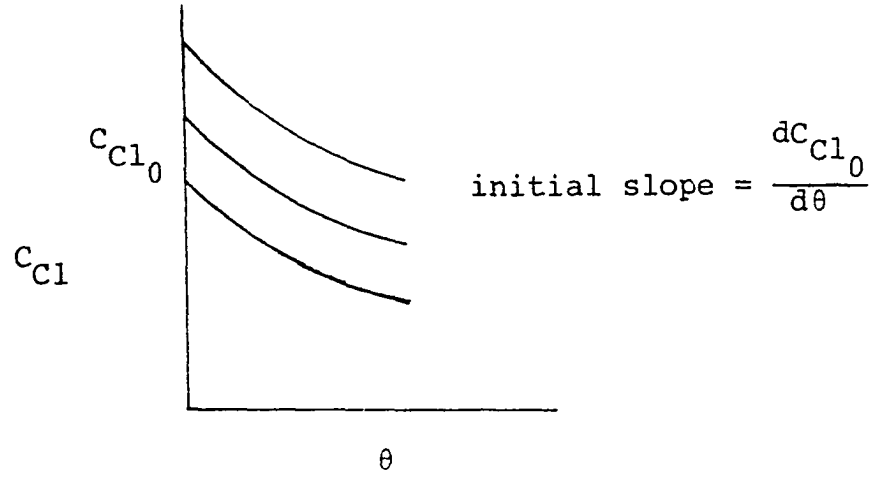
Then by plotting the slopes obtained from these curves the order of reaction β with respect to phosphoric acid concentration can be determined.

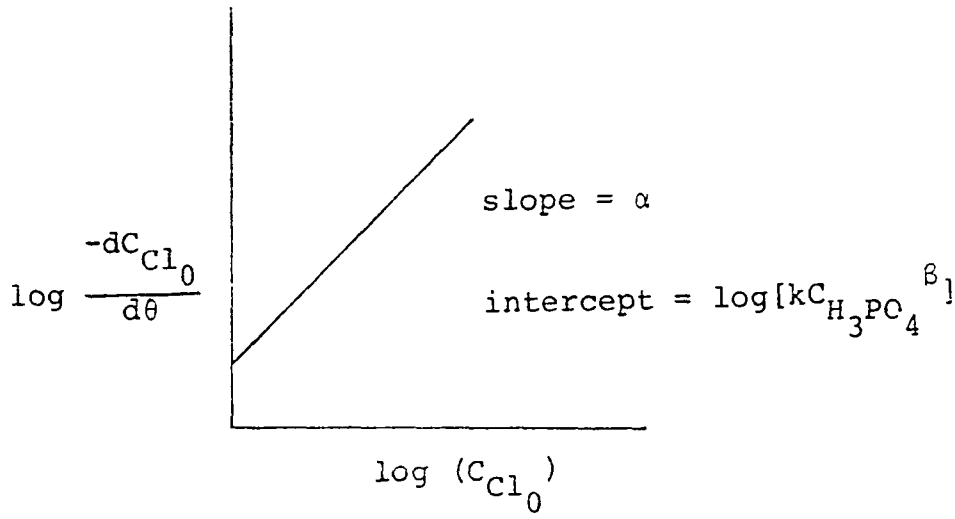
Figure 3. Schematic diagram of apparatus for measuring $KCl-H_3PO_4$ reactior


EXHAUST LINE
AIR LINE
HCl VAPOR
PYREX REACTION VESSEL
ROTAMETER
THERMO-REGULATOR
KCl-H_3PO_4 SOLUTION
ELECTRIC HEATING JACKET
AUTOMATIC TEMPERATURE CONTROLLER (RELAY AND RHEOSTAT)
AIR SPARGER

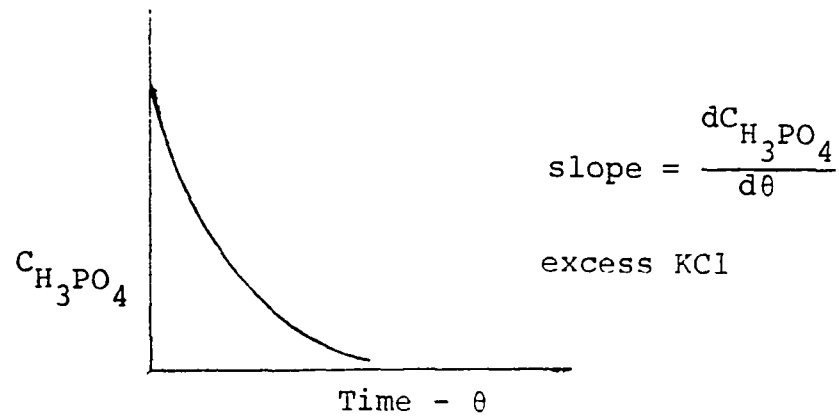


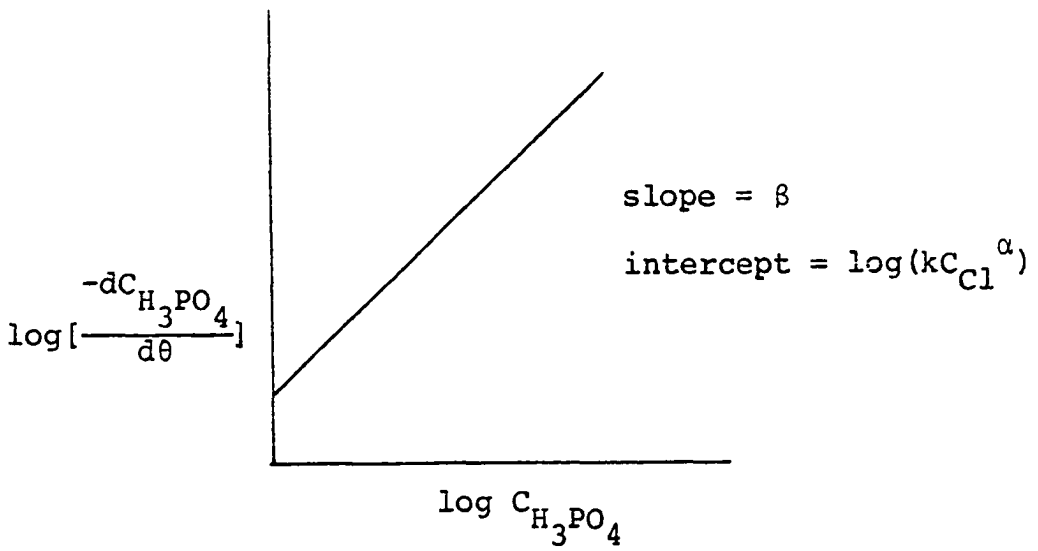
Likewise the order of reaction α with respect to potassium chloride concentration can be determined by plotting the initial concentrations of chloride versus time.



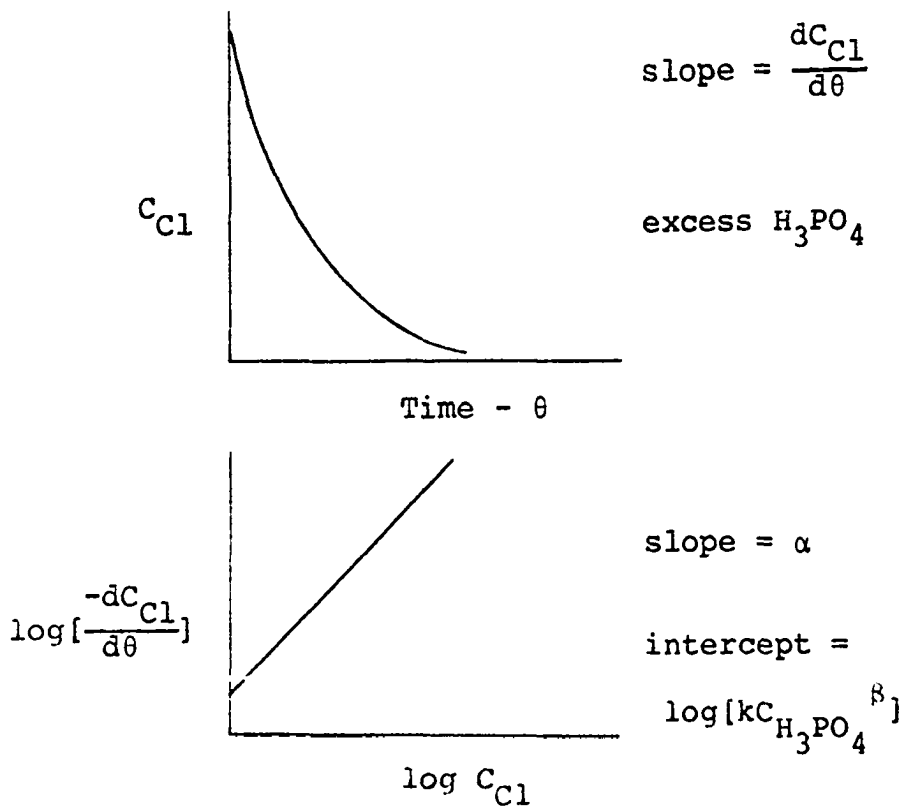


An alternative method of calculating α and β using a large excess of one reactant is as follows:





Thus β is obtained as the slope of the second graph. The value of α is obtained similarly.

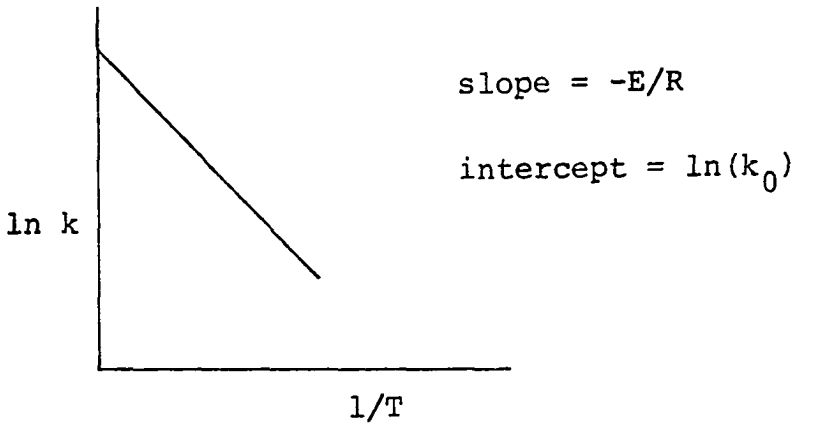


The values of k_0 the frequency factor and E the activation energy can be determined experimentally by obtaining values of k for various temperatures and plotting as shown below.

$$k = k_0 e^{-(E/RT)}$$

$$\ln(k) = \ln(k_0) + \ln(e^{-E/RT})$$

$$\ln(k) = \ln(k_0) - (E/RT)$$



The assumption that the reverse reaction is negligible is inaccurate for an endothermic reaction at low temperatures.

The assumed mechanism of the reaction is:

$$KCl_{aq} + H_3PO_{4aq} \rightleftarrows KH_2PO_{4aq} + HClaq$$

however, the rate of mass transfer of hydrochloric acid from the liquid phase to the gaseous phase may be the real rate controlling process for this reaction. Although the above

reaction may be the main reaction, several other simultaneous reactions may also be occurring such as:

$$2KH_2PO_4 \rightleftarrows K_2H_2P_2O_7 + H_2O$$

$$KCl + KH_2PO_4 \rightleftarrows K_2HPO_4 + HCl$$

$$K_2H_2P_2O_7 \rightleftarrows 2KPO_3 + H_2O$$

Each of these reactions could interfere to some extent with the kinetic measurements.

Due to the uncertainties of the purely theoretical approach of the kinetics of the KCl- H_3PO_4 reaction, a statistically designed series of experiments was carried out to determine the effects of four independent variables: aeration rate, residence time, temperature, and H_3PO_4-KCl reactant ratio. Using a Factorial experimental design technique the effect of each variable alone can be determined with a minimum of experimental data. Based on the information derived from this experimental design, the experimental objectives and procedures were accordingly altered to obtain the most meaningful results. If the statistical results of the experimental design had indicated the variable aeration rate was the most significant variable, that would mean that the rate of mass transfer of hydrochloric acid from the liquid phase to the gas phase may be

the controlling mechanism. Thus a less theoretical approach to the process kinetics could be undertaken. One such approach to the problem would be to measure the rate of reaction as a function of an individual variable while holding the other variables constant. Accordingly, curves indicating the rate versus time could be obtained for various levels of temperature, aeration rate, and H_3PO_4/KCl reactant ratio where these latter variables would be used as parameters.

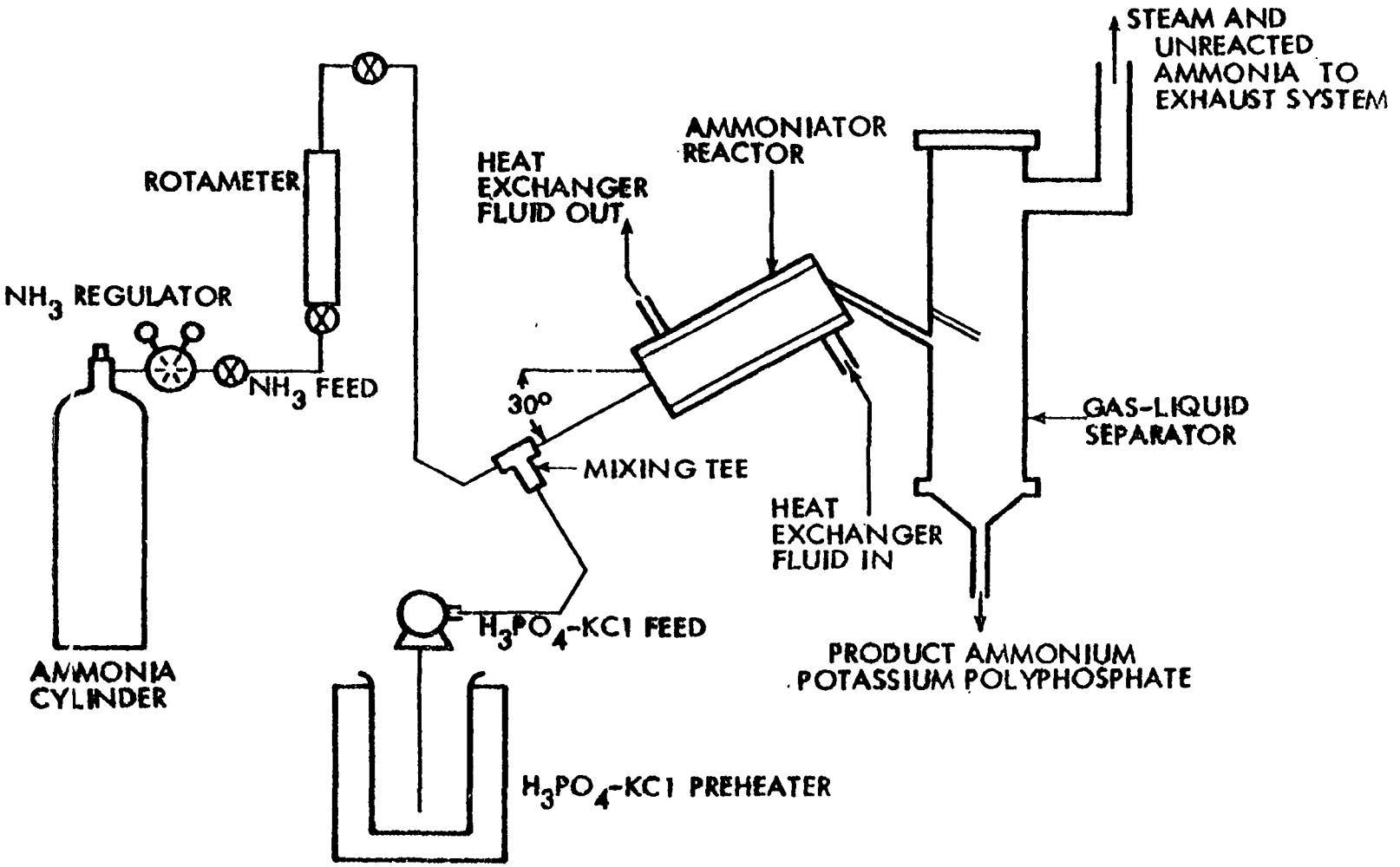
For the ammoniator reactor used in this work the range of feed and operating conditions which would produce a satisfactory ammonium potassium polyphosphate product was not known. Also, whether the reversion of phosphate to an unavailable form would be encountered was not known. Therefore optimum operating conditions with respect to product analysis were determined. The degree of flexibility in nutrient formulation was determined. Due to the lower viscosities it was expected that the low K/P mole ratio products would be more easily processed in the ammoniator than the higher ratio products. The production of products with ratios of 1:2.5:0 and 1:2.5:2 (elemental basis) were attempted. The operating conditions of this ammoniator reactor were determined for the two formulations. The effects of feed temperature, reactor temperature, reactor

pressure, and residence time all have an effect upon the reaction and therefore affect the chemical analysis of the products. It was expected that reactant feeds producing a low K/P ratio (also high N:P ratio) would require external cooling to maintain the ammoniator at a satisfactory operating temperature; whereas, the reactant feeds producing a high K/P ratio product (low N:P ratio) might require some type of external heating, such as preheating the reactants, in order to reach a high enough reaction temperature. Intermediate range products with ratios such as 1-3-1 might not require external heating or cooling for the ammoniator reactor since the heat of reaction could be sufficient to both produce a complete reaction and also dehydrate the resulting products. Enthalpy balances are shown for several reactions in Appendix A.

Materials

Phosphoric acid 85% reagent grade, Matheson Coleman & Bell
Potassium hydroxide USP pellets, Matheson Coleman & Bell
Potassium chloride USP granular, Mallinckrodt
Anhydrous Ammonia from cylinder, Matheson Co.

Figure 4. Polyphosphate ammoniator reactor system


STEAM AND
UNREACTED
AMMONIA TO
EXHAUST SYSTEM
AMMONIATOR
REACTOR
HEAT
EXCHANGER
FLUID OUT
ROTAMETER
NH3 REGULATOR
NH3 FEED
30°
MIXING TEE
GAS-LIQUID
SEPARATOR
HEAT
EXCHANGER
FLUID IN
H3PO4-KCl FEED
AMMONIA
CYLINDER
PRODUCT AMMONIUM
POTASSIUM POLYPHOSPHATE
H3PO4-KCl PREHEATER

Description of Equipment

Apparatus for measuring $KCl-H_3PO_4$ reaction kinetics

The equipment used for the experimental measurement of the kinetics of the $KCl-H_3PO_4$ reaction is shown in Figure 3. A two liter pyrex reaction vessel was used to react potassium chloride and phosphoric acid. This vessel was heated by a 470 watt electric heating jacket. The reaction temperature was controlled through the use of a mercury thermoregulator in conjunction with a relay, rheostat and the heating jacket. Temperatures could be controlled with an accuracy within one degree centigrade. An air sparger with a gas dispersion stone was used to purge the reaction system of hydrochloric acid. Various volumetric flow rates were maintained by passing the incoming air through a rotameter. Air flow rates could be varied from zero to one thousand cubic centimeters per minute. For agitation a glass stirring rod in an oval shape was used to insure intimate mixing of the reactants.

Ammonium potassium polyphosphate reactor

The ammonium potassium polyphosphate reactor and auxiliary equipment is shown in Figures 4 through 10.

Product from the $KCl-H_3PO_4$ reaction was not used in the polyphosphate reactor. A $H_3PO_4-KH_2PO_4$ solution made from KOH and H_3PO_4 was used. The actual reaction between ammonia

Figure 5. Ammoniator reactor

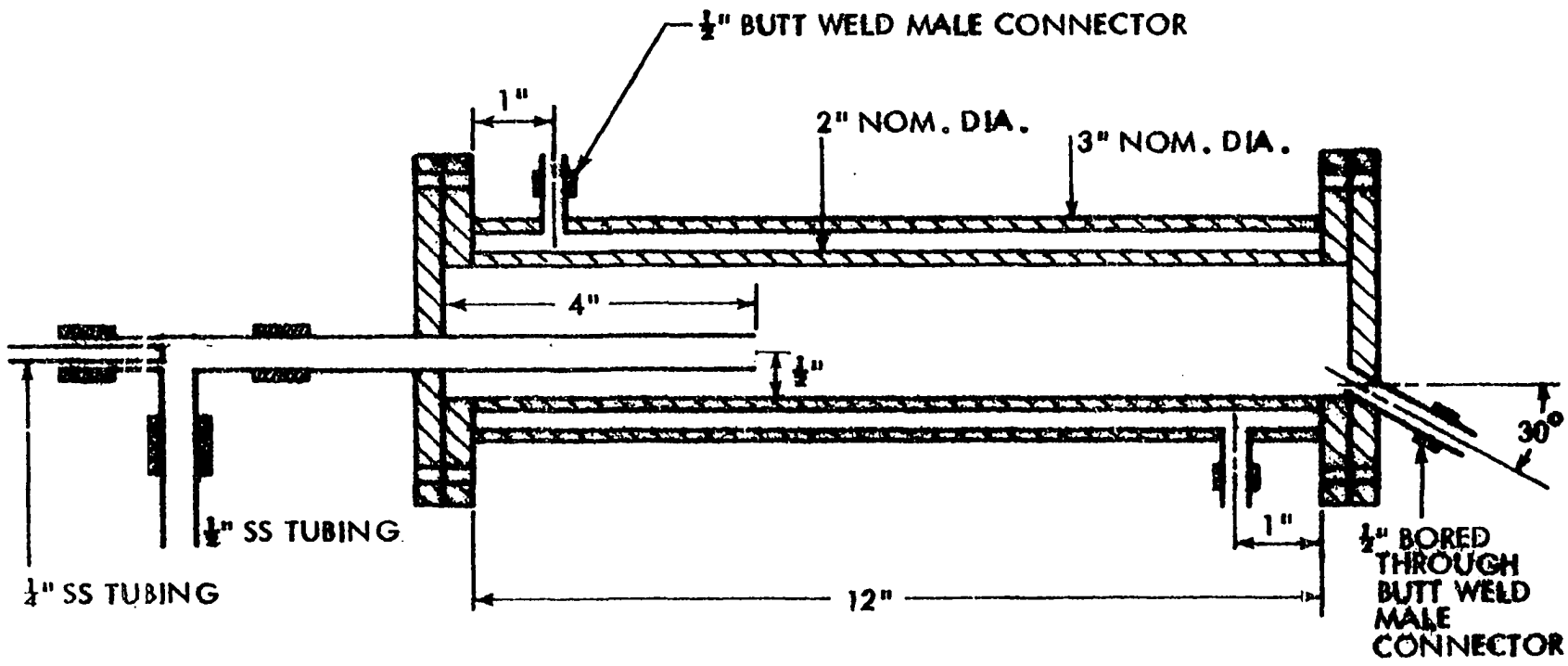

½" BUTT WELD MALE CONNECTOR
1"
2" NOM. DIA.
3" NOM. DIA.
4"
½"
30°
¼" SS TUBING
¼" SS TUBING
1"
½" BORED THROUGH BUTT WELD MALE CONNECTOR
12"

Figure 6. Gas-liquid separator

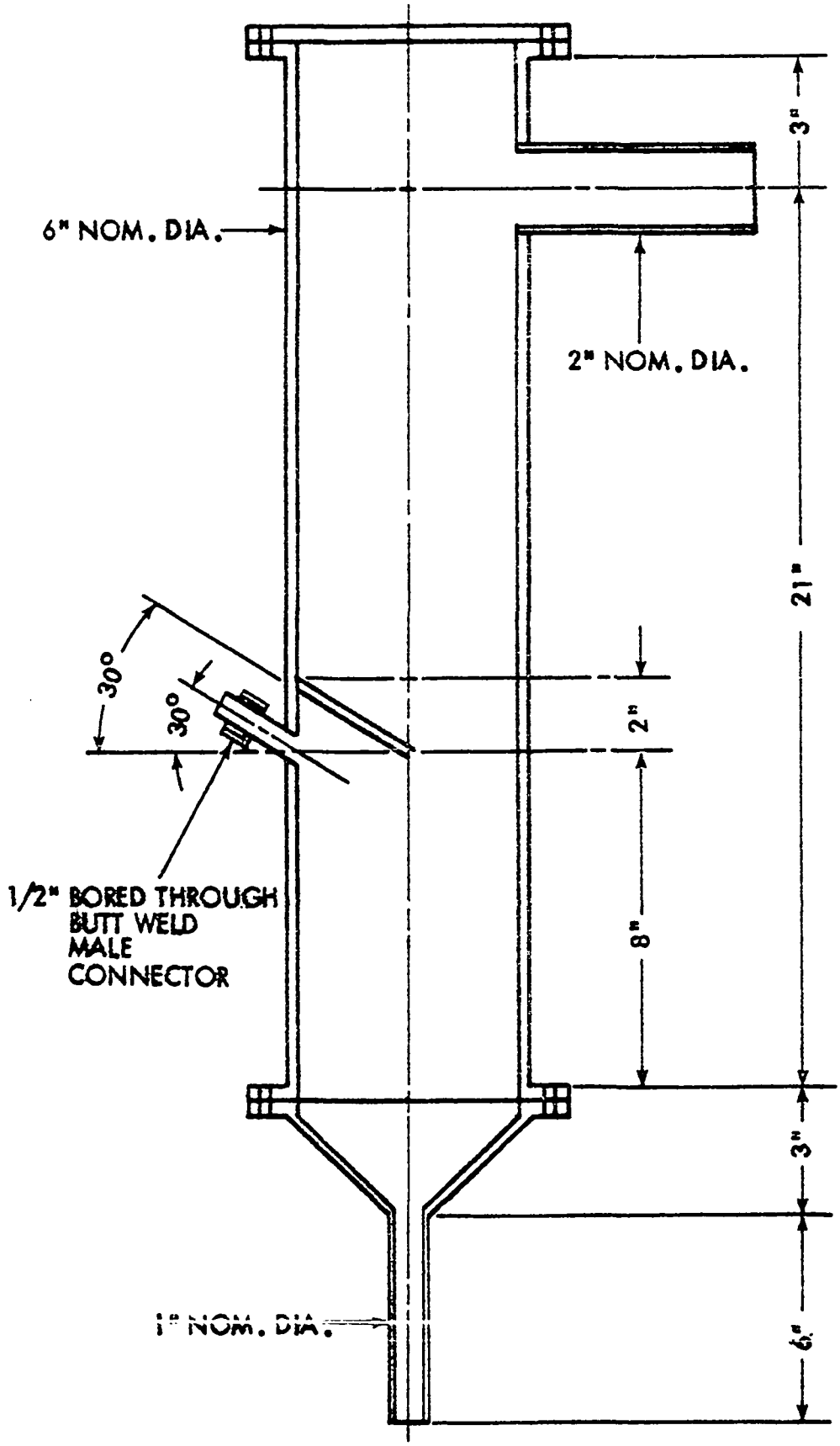
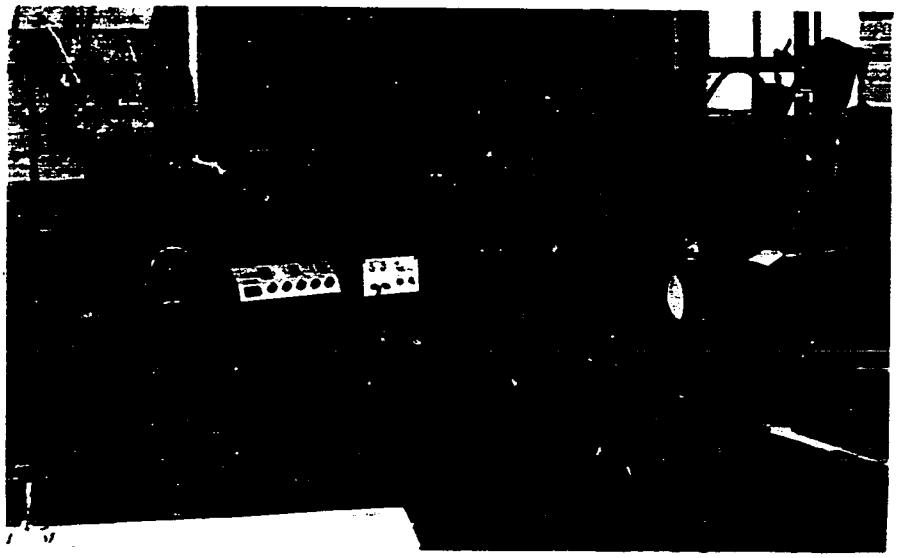

6" NOM. DIA.
2" NOM. DIA.
3"
21"
30°
30°
2"
8"
1/2" BORED THROUGH
BUTT WELD
MALE
CONNECTOR
3"
1" NOM. DIA.
6"

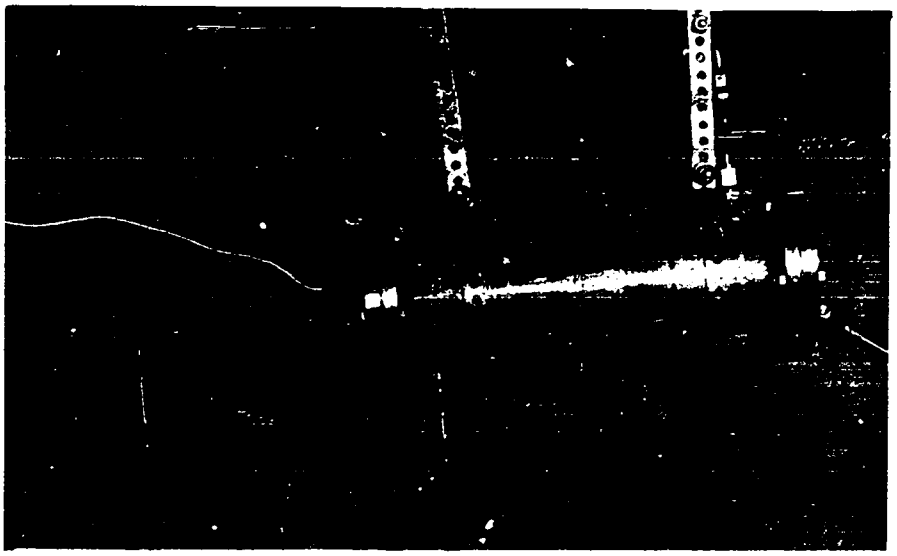
Figure 7. Experimental polyphosphate ammoniation apparatus

Figure 8. Experimental polyphosphate ammoniation apparatus without insulation

Figure 9. Front view of polyphosphate ammoniation apparatus

Figure 10. Ammoniator reactor





and the H_3PO_4-KH_2PO_4 solution took place in the mixing tee in the reactor shown in Figure 5. It was found necessary to remove the baffles in the reactor in order to prevent freezing of the product inside the reactor. It was also necessary to withdraw the inside ammonia feed line (Figure 5) to a position such that the ammonia outlet was at the center of the mixing tee.

The reactor and all feed lines were made of 316 stainless steel. The reactor was built to withstand high pressures, high temperatures and the corrosiveness of the reactants and products.

The heat exchanger surrounding the reactor utilized a Ucon heat exchanger fluid in order to heat the reactor initially and to cool and maintain a given reactor temperature during the reaction. This exchanger fluid was heated to a maximum temperature of 232°C. by means of a thermostatically controlled electrical resistance heater system (3000 watts).

The feed lines for ammonia and H_3PO_4-KH_2PO_4 solution, and the product line were heated by means of electrical heating tapes. Proper temperatures were monitored through four iron constantan thermocouples. The pressure in the ammoniator reactor was measured by a piezoelectric pressure transducer in conjunction with a charge amplifier and a cathode ray oscilloscope. The oscilloscope was calibrated

to read directly in pounds per square inch from zero to one hundred.

Ammonia under pressure from a cylinder was fed to the mixing tee through one quarter inch 316 stainless steel tubing. The ammonia flow rate was measured by a calibrated rotameter. After passing through the rotameter the ammonia was heated and vaporized by electrical heating tapes before entering the mixing tee. Several valves including a safety check valve were employed to prevent any backflow of ammonia or other reactants into the ammonia line or cylinder both during the reaction process and afterwards.

The phosphoric acid-monopotassium orthophosphate melt feed was maintained in a liquid form in a heated ten liter stainless steel beaker. The feed vessel was automatically controlled with respect to temperature with a 1000 watt electric heating mantle, relay, rheostat, and mercury thermoregulator. This feed material was pumped to the mixing tee by a teflon diaphragm pump. The liquid melt flow rates could range up to a maximum of thirty pounds per hour. Heating tapes were also used in heating and maintaining the temperature of the acid melt as it passed to the mixing tee before reacting with the ammonia.

After the reaction the product melt passed from the reactor to the gas-liquid separator, Figure 6. Again heating tapes were employed in keeping the molten product in the

liquid form during transfer. The gas-liquid separator made of 316 stainless steel was six inches in diameter and two feet high. Product steam and unreacted ammonia were exhausted at the top of the gas-liquid separator into a steam exhaust system. The product ammonium potassium polyphosphate melt flowed by gravity out the base of the gas-liquid separator.

The temperatures of the various feed and product lines maintained by the heating tapes were controlled by rheostats. The temperatures of these various lines were measured with thermocouples and a potentiometer. The use of heating tapes for maintaining feed line temperatures was satisfactory as long as feed material was continuously flowing through them. However, changes in feed rates or interruptions in the process required readjustments in the rheostat settings.

Experimental Method

H_3PO_4-KCl reactor

Using the apparatus as shown in Figure 3, batch experiments were performed according to a 2^4 factorial experimental design. The four variables were each assigned different levels as follows.

a_0, a_1 = temperature 110°C, 140°C

b_0, b_1 = retention time 10 min., 30 min.

c_0, c_1 = aeration rate 0 cc/min., 500 cc/min.

d_0, d_1 = H_3PO_4/KCl reactant ratio 1.33, 2.00

An analysis of variance table was made using the results obtained from the experimental design. The significance of the single variables upon the reaction rate were determined and also the significance of the two factor interactions. These results are shown in Appendix B.

After analyzing the results of the preliminary statistical experimental design and taking into consideration the effect of the factors A, B, C and D upon the reaction, the following conditions were selected for the determination of the reaction rate kinetics of the H_3PO_4-KCl reaction.

Factor A - Temperature	100 to 160°C
Factor B - Retention time	0 to 30 minutes
Factor C - Aeration rate	none
Factor D - H_3PO_4-KCl reactant ratio	3.33 to 20.0

The values of α and β, the reaction rate orders, were both determined using the differential method shown earlier.

The value of α was determined using both the standard differential method and the method of varying initial KCl concentrations. The latter method gave much more reliable results and was carried out at two different temperatures; 120°C. and 140°C. The value of β was determined using a large excess of KCl with a H_3PO_4:KCl reactant ratio equal to 0.10

again using the standard differential method. However, changes in the chloride concentration of the reacting solution could not be determined accurately. Therefore, the change in chloride content was measured by collecting the evolving HCl vapors, neutralizing them and then quantitatively analyzing for chloride. This method involved a time delay between the time of reaction and time of HCl collection, but was much more accurate than direct analysis of the reacting solution. It was assumed the KCl and H_3PO_4 reacted in a one to one mole ratio as described in the kinetic rate expression. By quantitatively measuring the amount of HCl evolved as a function of time, the equivalent amount of H_3PO_4 that reacted was determined. The H_3PO_4 concentration thus obtained was used in the graphical determination of the reaction rate order β.

The reaction rate constant k was determined for the four different temperatures by solving the rate equation for k using the known values for reactant concentrations and the determined values for α and β.

The activation energy E was determined graphically by plotting the logarithm of the reaction rate constant k versus the reciprocal of the absolute temperature 1/T. The slope of the resulting curve, E/R, is used to calculate the activation energy E.

Ammoniator reactor

The apparatus used in the ammoniation of the H_3PO_4-KH_2PO_4 melt shown in Figure 4 was first tested using only ammonia. All lines and fittings were checked for gas leakage. Phosphoric acid was then pumped alone and the heating tapes tested. As a safety precaution the first ammoniation reaction was between dilute phosphoric acid and ammonia. The product froze in the ammoniator during the production of ammonium polyphosphate from 26% P feed acid. The ammoniator was then modified by removing the baffles; the ammonia feed line was withdrawn to form a mixing tee with the acid feed, and the temperatures of the reactor heat exchanger and of the product line were increased.

The optimum operating conditions for the maximum N/P mole ratio of the product were determined. First the effect of N/P feed ratio upon product composition was determined. This was done by using a fixed flow rate of H_3PO_4-KH_2PO_4 and increasing the ammonia feed rate in increments while collecting product samples. The N/P feed ratio ranged from zero to two. Other operating conditions were:

Pressure:	40 psi
Reactor temperature:	210°C
Calculated residence time:	2.61 min.
N/P mole feed ratio:	0.00 to 2.00

H_3PO_4-KH_2PO_4 flow rate:	7.1 liters per hour
Melt feed temperature:	175°C
Melt feed composition % K	16.5 %
% P	26.2 %

Product samples were collected in sample bottles with a measured amount of cold distilled water to prevent the loss of ammonia. The product was analyzed for total nitrogen, total phosphorus and potassium. The nitrogen to phosphorus ratio of the product was then calculated. Nitrogen content was determined by the direct Nesslerization method. Phosphorus was determined using the AOAC spectrophotometric vanadomolybdate method; whereas potassium was determined using the AOAC flame photometric method.

The effect of reactor temperature upon product composition was determined. The reactor temperature was controlled by changing the temperature of the heat exchanger fluid surrounding the ammoniator reactor. This was varied from 177 to 232 degrees Centigrade. The temperature in this case was limited by the heat exchanger fluid. At temperatures above 232°C the heat exchanger fluid would smoke and begin to decompose. The other operating conditions, while measuring the effect of reactor temperature upon product composition, are shown below.

Pressure:	40 psi
Reactor temperature:	177 to 232°C

Calculated residence time:	2.61 minutes
N/P mole feed ratio:	1.00
H_3PO_4-KH_2PO_4 flow rate:	7.1 liters per hour
Melt feed temperature:	177°C
Melt feed composition % K	16.5 %
% P	26.2 %

The effect of pressure upon the product composition was also determined. The pressure was controlled by regulating the product outlet flow rate. However, pressure fluctuations of up to ten pounds per square inch occurred. The pressure in the ammoniator reactor was varied up to seventy-five pounds per square inch. Pressures above eighty pounds per square inch could not be achieved due to the limited pressure head that could be developed by the melt feed pump. It is believed that a change in the reactor pressure would also affect the calculated residence time. Since the calculated residence time was based on fifty percent liquid and fifty percent gases in the ammoniator reactor, different proportions of liquid and gases due to different pressures could thus alter the calculated residence time. The operating conditions for measuring the effect of pressure upon product composition are shown below.

Pressure:	0 to 75 psi
Reactor temperature:	210°C
Calculated residence time:	2.61 min.

N/P mole feed ratio:	1.00
H_3PO_4-KH_2PO_4 melt flow rate:	7.1 liters per hour
Melt feed temperature:	177°C
Melt feed composition % K	16.5 %
% P	26.2 %

Residence time during the ammoniation reaction was calculated by dividing one half of the ammoniator reactor's volume by the volumetric flow rate of the H_3PO_4-KH_2PO_4 melt. The volume of the ammonia was neglected. To measure the effect of residence time upon product composition the feed rates of both the H_3PO_4-KH_2PO_4 and ammonia were correspondingly decreased. The operating conditions shown below were used in determining the effect of residence time upon product composition.

Pressure:	40 psi
Reactor temperature:	210°C
Calculated residence time:	2.61 to 6.18 minutes
N/P feed mole ratio:	1.00
H_3PO_4-KH_2PO_4 melt flow rate:	3.0 to 7.1 liters per hour
Melt feed temperature:	177°C
Melt feed composition: % K	16.5 %
% P	26.2 %

RESULTS AND DISCUSSION OF RESULTS

H_3PO_4-KCl reactor:

The experimental reaction rate kinetics of the following equation were determined.

$$KCl + H_3PO_4 \rightarrow KH_2PO_4 + HCl$$

The reverse reaction was neglected to give the rate expression of:

$$\frac{-dC_{Cl}}{d\Theta} = k_0 e^{-E/RT} [C_{Cl}] [C_{H_3PO_4}]^{\beta}$$

Using the standard differential method the value of α the order of the reaction with respect to the chloride concentration could not be determined accurately. The graphical technique employed in this method resulted in a curve yielding a large variance in the value of α as a function of time. This was due to the effect of the reverse reaction increasingly affecting the reaction rate as the time of reaction increased.

More accurate measurements of α were obtained by varying the initial concentration of chloride and only determining the initial reaction rate as a function of chloride concentration, (Figures 11 and 12). Using an excess of phosphoric acid, the experimental values of α were

Figure 11. Reaction rate - chloride concentration versus time at 120°C

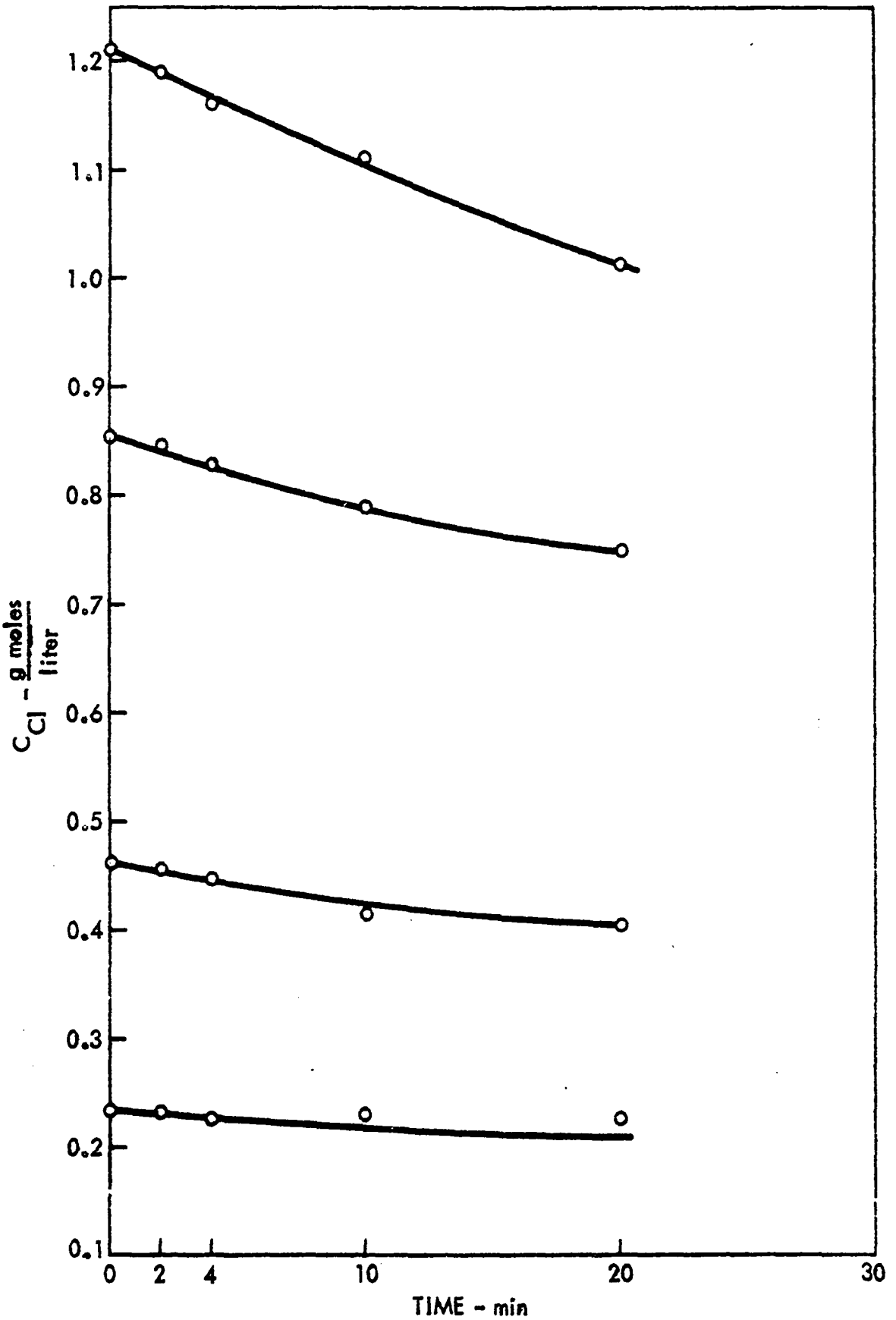
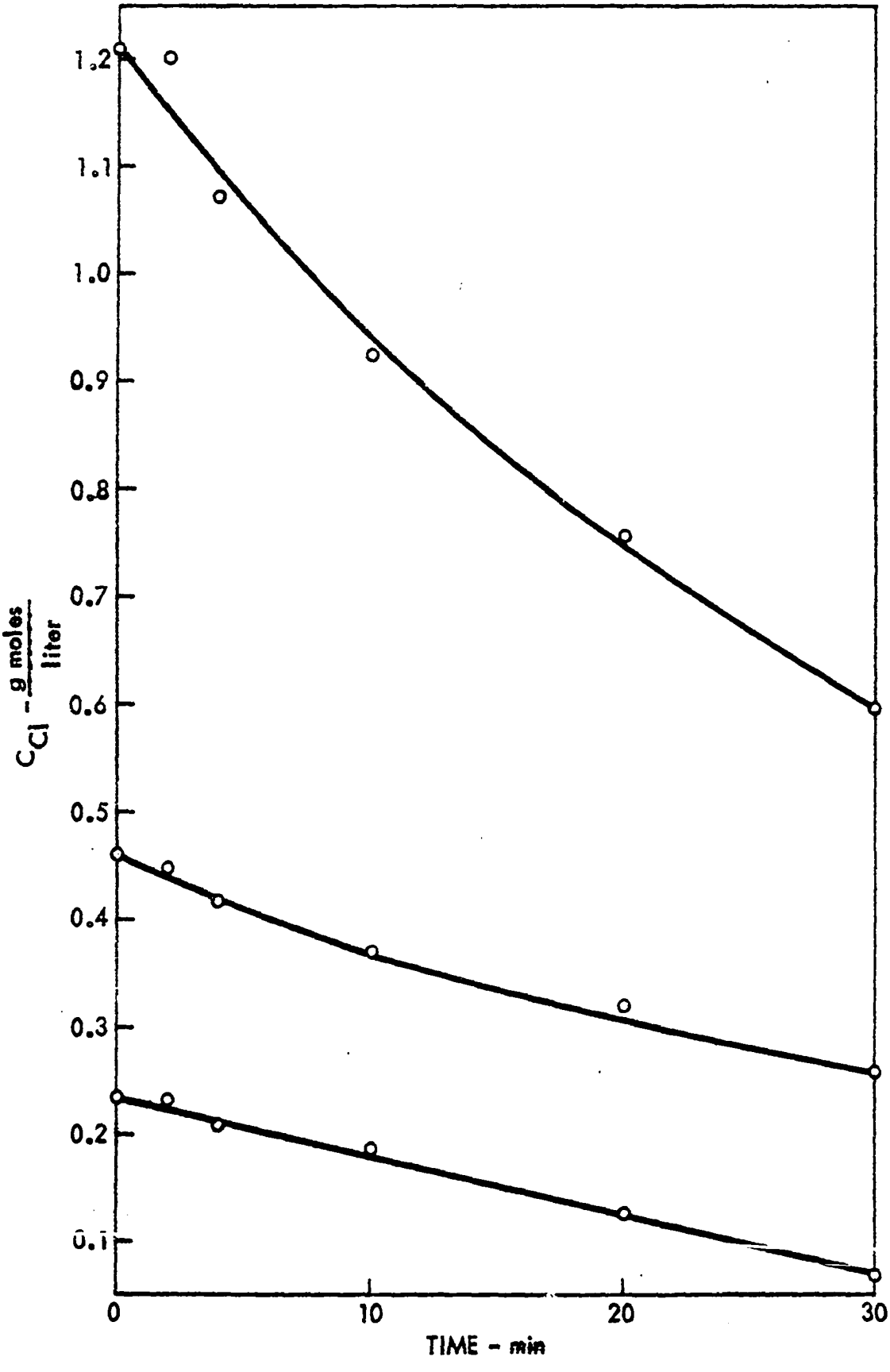

1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
C_{Cl} - g moles / liter
0
2
4
10
20
30
TIME - min

Figure 12. Reaction rate - chloride concentration versus time at 140°C


1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
C_{Cl} - g moles / liter
0
10
20
30
TIME - min

found to be 1.15 at 120°C and 1.01 at 140°C, (Figure 14). For further analytical calculations the value of α was assumed to be 1.00. A large amount of data was required in determining α using the modified differential method of varying the initial chloride concentrations. Therefore, β, the reaction rate order with respect to phosphoric acid concentration, was determined using the less accurate standard differential method. In order to improve the accuracy in the determination of β, a large number of samples were collected in the thirty minute period of reaction (Figure 16). The value of β varied from 0.87 at time zero to greater than 4.0 at time twenty minutes after the reaction commenced. The increase in reaction rate order again would be expected to be due to the increasing effect of the reverse reaction upon the reaction kinetic expression with increasing time. It would be expected that the initial value of β at time zero would be somewhat low due to the time delay in the collection of the evolving HCl vapors used in the analytical measurements. This latter inaccuracy was not encountered in the measurement of α since the reaction system was directly sampled for chloride concentration. The most accurate value of β would be obtained at time zero; therefore, the true value of β should be somewhat close to the 0.87 measured. Again for further calculation purposes the value of β was assumed to be

1.00.

The activation energy for the forward reaction was experimentally determined to be 18,088 calories per gram mole from Figure 15. Whereas, the theoretical heat of reaction is -16,820 calories per gram mole. The value of the frequency factor k was experimentally determined to be 2.72×10^6 liter minutes per gram mole. In conclusion the final rate expression for the forward reaction based on the results of the experimental analysis was set at:

$$-\frac{dC_{Cl}}{d\theta} = k_0 e^{-E/RT} [C_{Cl}]^{\alpha} [C_{H_3PO_4}]^{\beta}$$

$$-\frac{dC_{Cl}}{d\theta} = (2.72 \times 10^6 \frac{1.min.}{gm.mole}) (e^{-\frac{18,088 cal/gm.mole}{RT}})$$

$$[C_{Cl}]^{1.0} [C_{H_3PO_4}]^{1.0}$$

Ammoniator reactor:

The degree of ammoniation of molten H_3PO_4-KH_2PO_4 was experimentally determined as a function of N/P feed mole ratio, temperature, pressure, and residence time. These results are shown graphically in Figures 19 through 23 and in tabular form in Appendix D.

A N/P feed mole ratio of 1.00 was used in all cases except when the effect of N/P feed mole ratio upon product composition was determined. The results shown in Figures 19 and 20 indicate that less than seventy percent of the ammonia

Figure 13. Reaction rate - chloride concentration versus time at 100° and 160°C

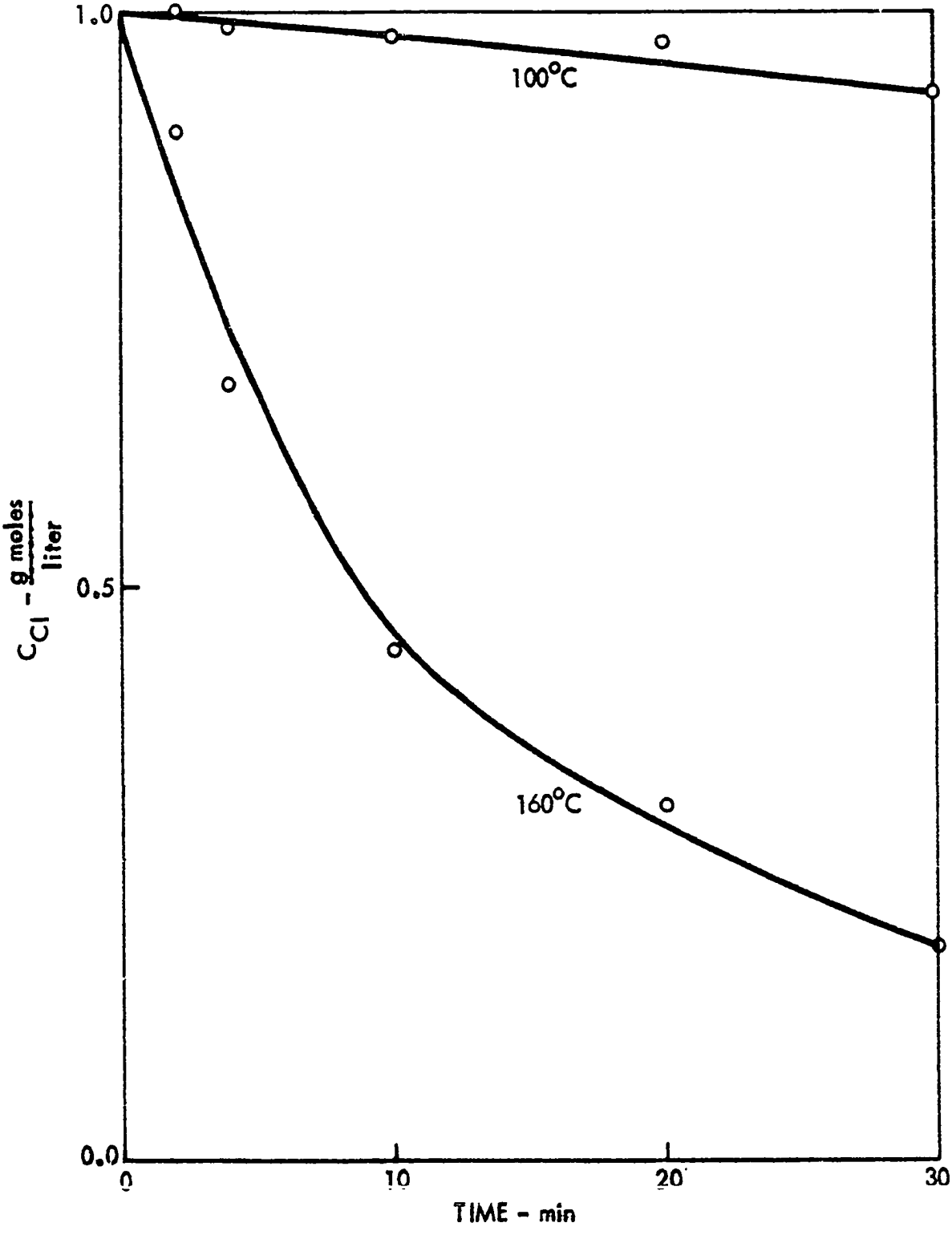

1.0
0.5
0.0
100°C
160°C
0
10
20
30
TIME - min
C_{Cl} - g moles / liter

Figure 14. Determination of reaction rate order

$$-\ln\left[\frac{-dC_{Cl_0}}{d\theta}\right] \text{ versus } \ln[C_{Cl_0}]$$

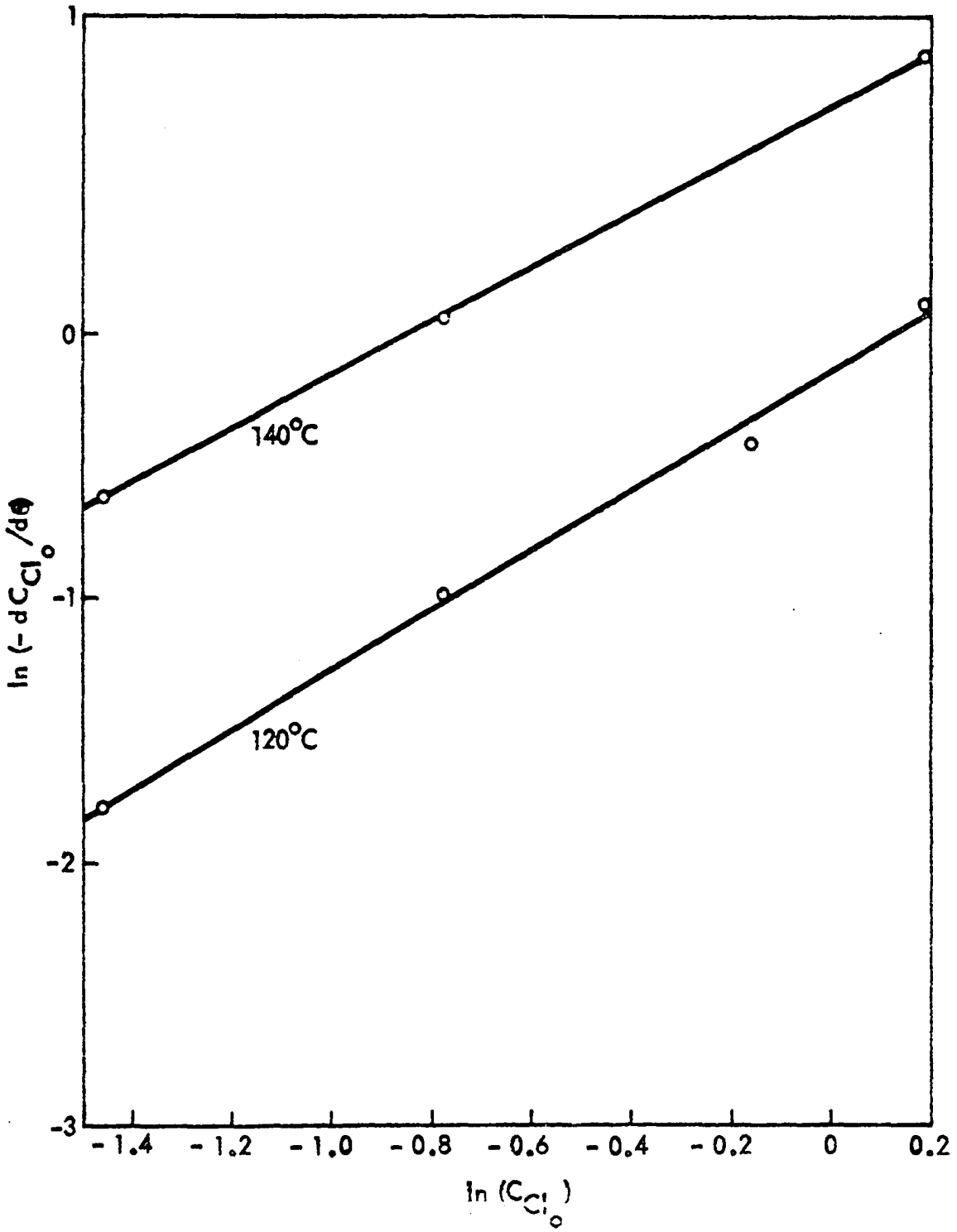

1
0
-1
-2
-3
140°C
120°C
$\ln(-dC_{Cl_2}/d\theta)_o$
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
0.2
$\ln(C_{Cl_2})_o$

Figure 15. Determination of activation energy - ln k versus 1/T

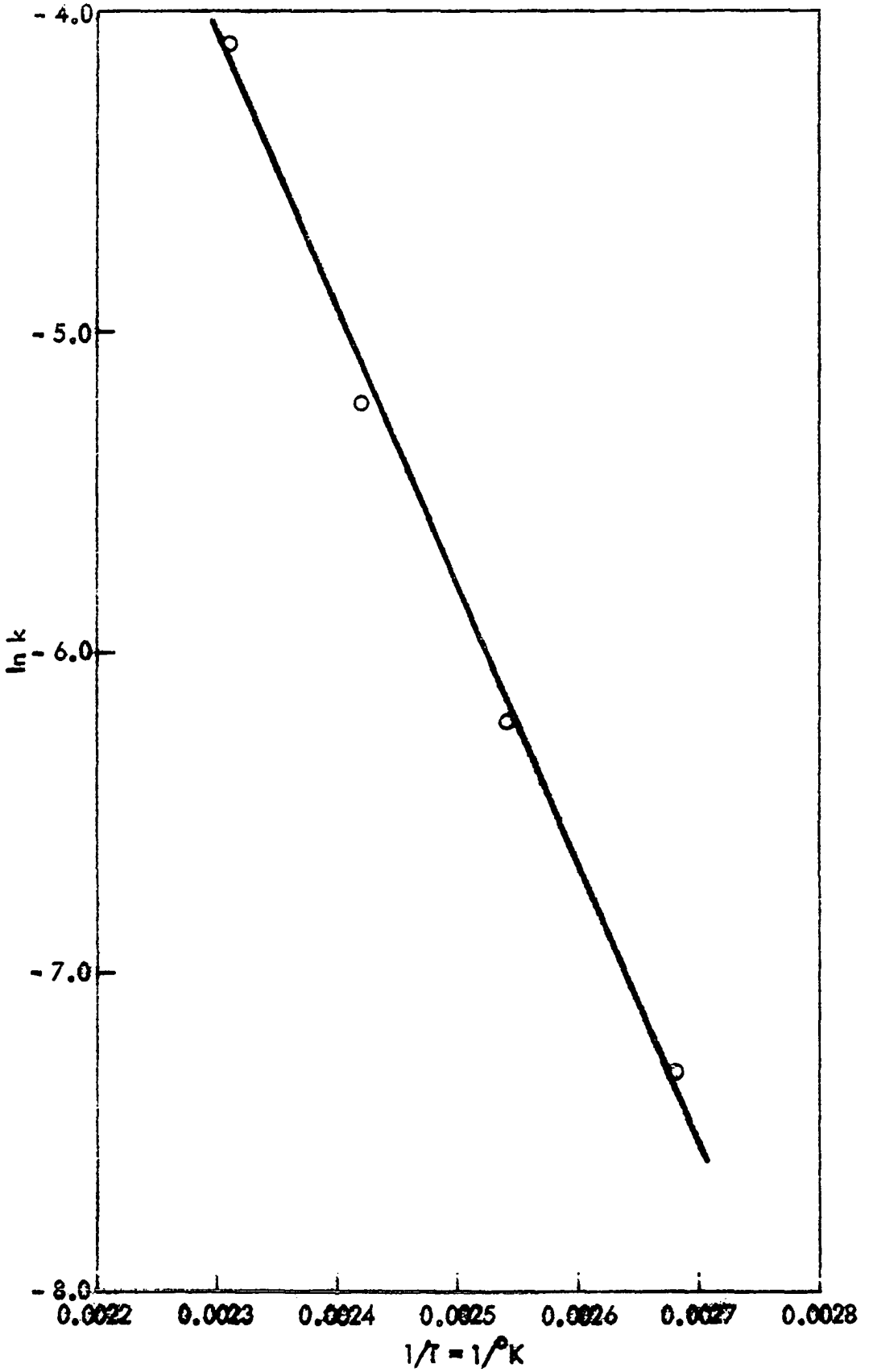

- 4.0
- 5.0
- 6.0
- 7.0
- 8.0
ln k
0.0022
0.0023
0.0024
0.0025
0.0026
0.0027
0.0028
1/T = 1/°K

Figure 16. Reaction rate - phosphoric acid concentration versus time

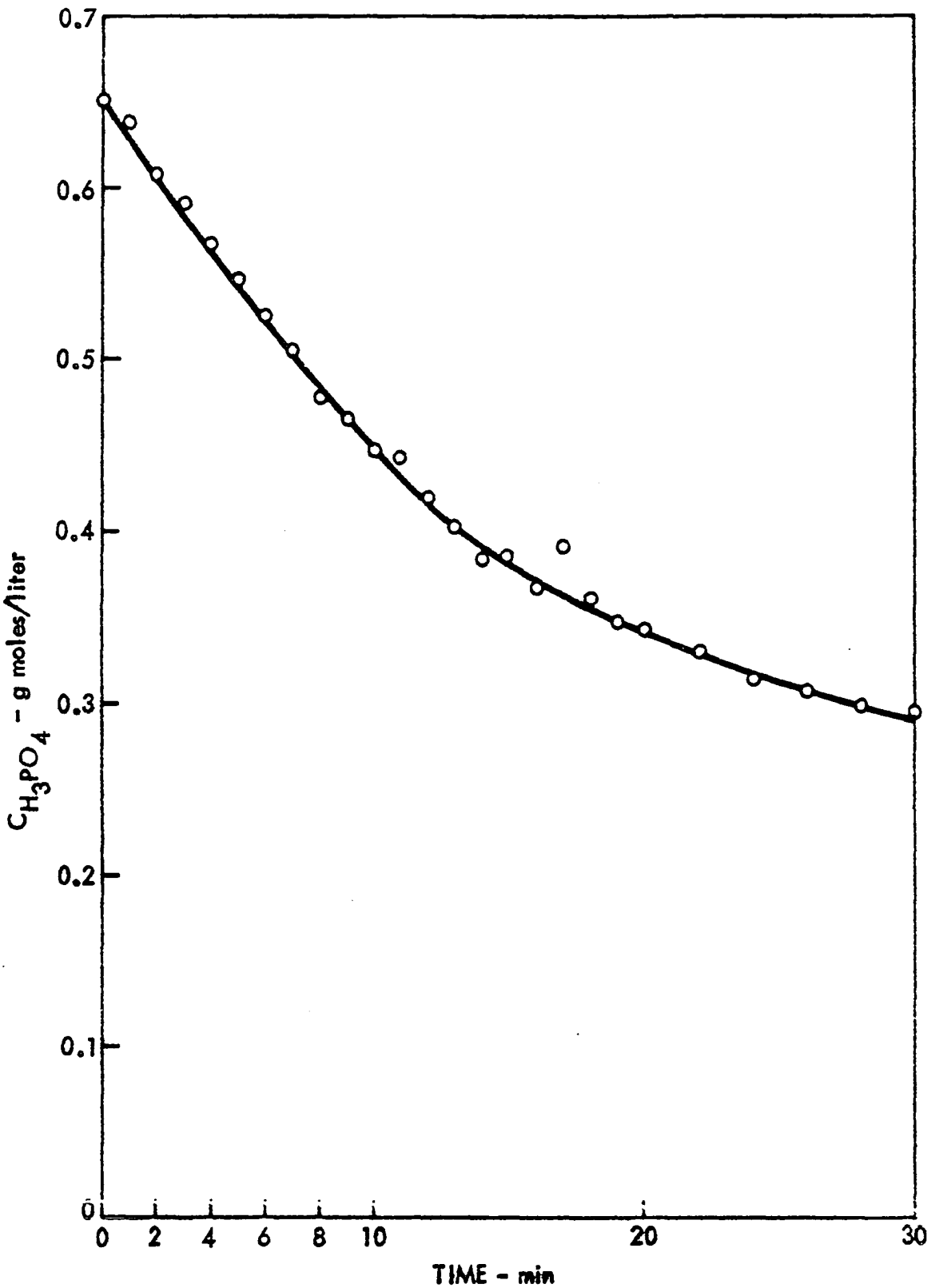

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
$C_{H_3PO_4}$ - g moles/liter
0
2
4
6
8
10
20
30
TIME - min

Figure 17. Determination of reaction rate order

$$-\ln\left[\frac{-dC_{H_3PO_4}}{d\theta}\right] \text{ versus } \ln[C_{H_3PO_4}]$$

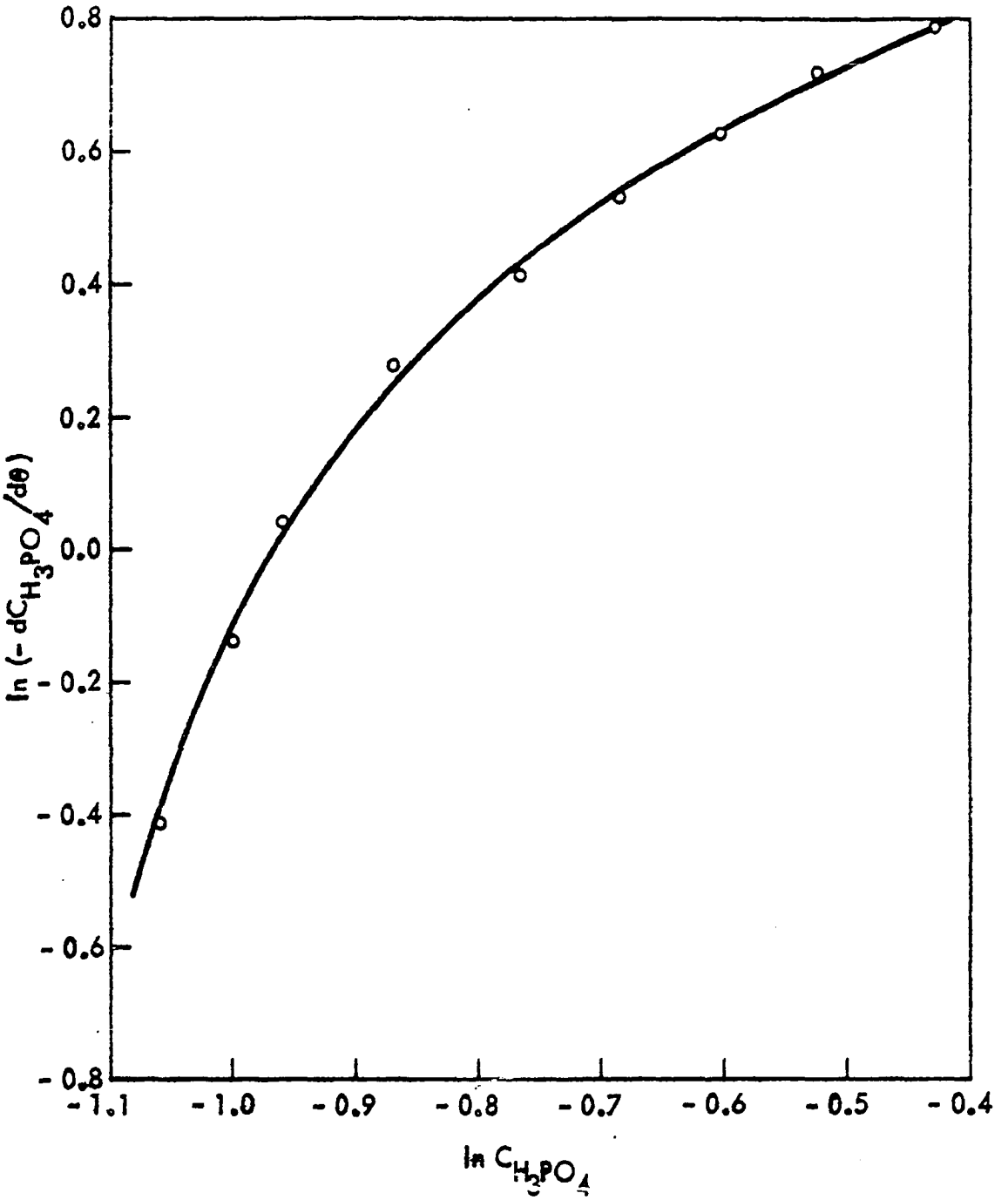

0.8
0.6
0.4
0.2
0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.1
- 1.0
- 0.9
- 0.8
- 0.7
- 0.6
- 0.5
- 0.4
ln (- dC$_{H_3PO_4}$/dθ)
ln C$_{H_3PO_4}$

Figure 18. Reaction rate constant as a function of temperature - k versus temperature

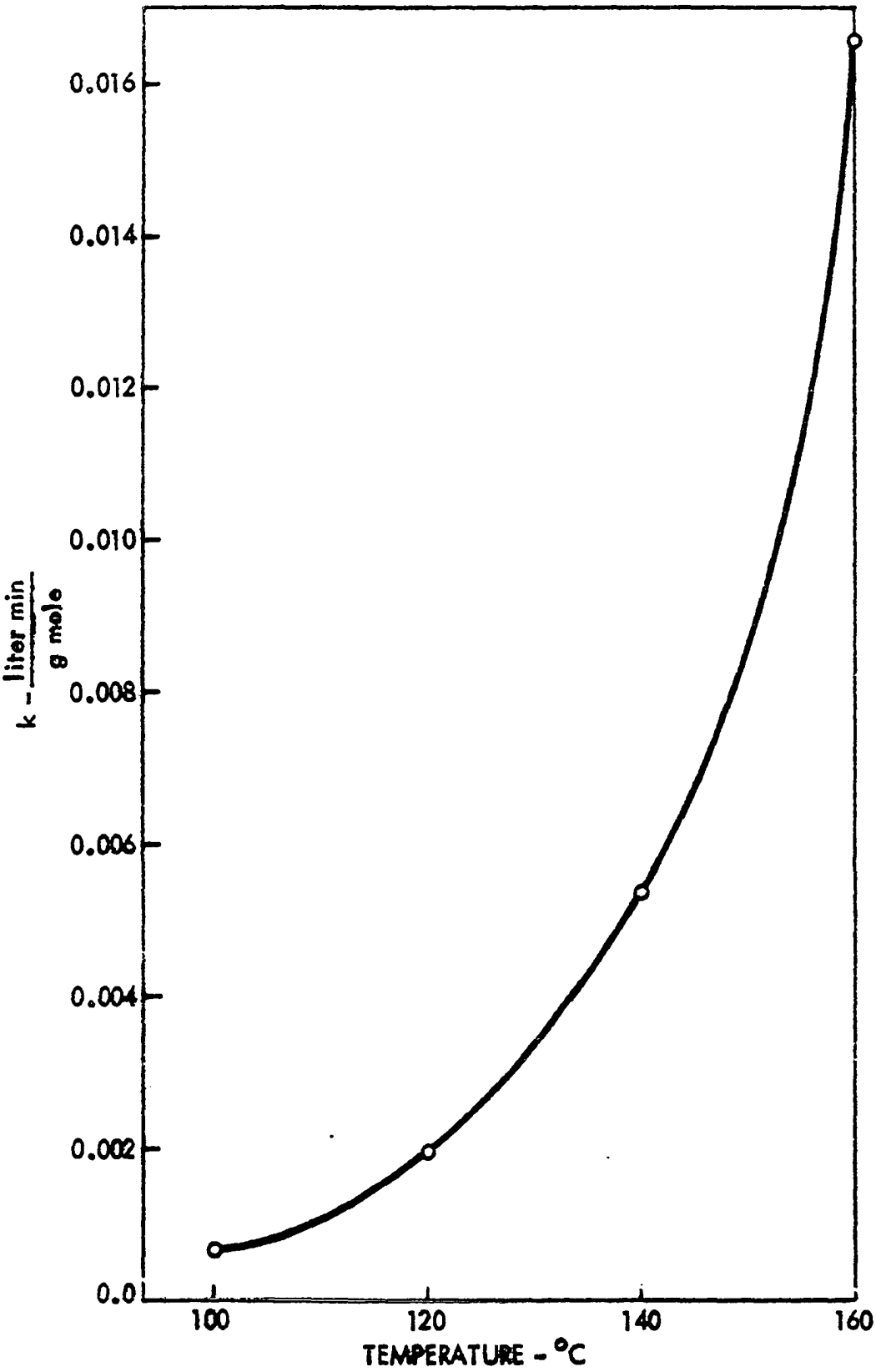

0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.0
k - liter min / g mole
100
120
140
160
TEMPERATURE - °C

Figure 19. Ammonia efficiency - percent ammonia reacted versus N/P feed mole ratio

Figure 20. Degree of ammoniation of product as a function of ammonia input - N/P product mole ratio versus N/P feed mole ratio

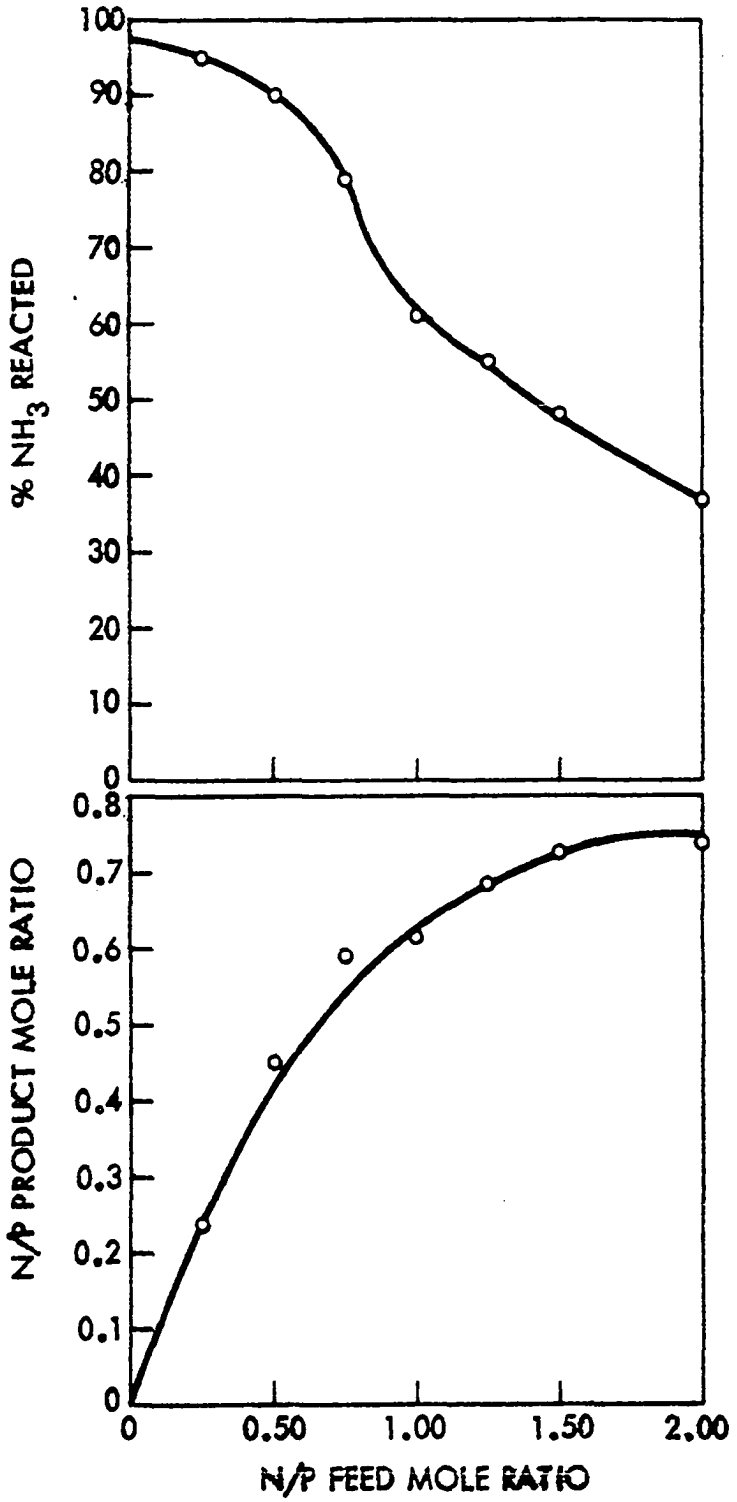

% NH_3 REACTED
100
90
80
70
60
50
40
30
20
10
0
N/P PRODUCT MOLE RATIO
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.50
1.00
1.50
2.00
N/P FEED MOLE RATIO

Figure 21. Degree of ammoniation as a function of temperature - N/P product mole ratio versus temperature

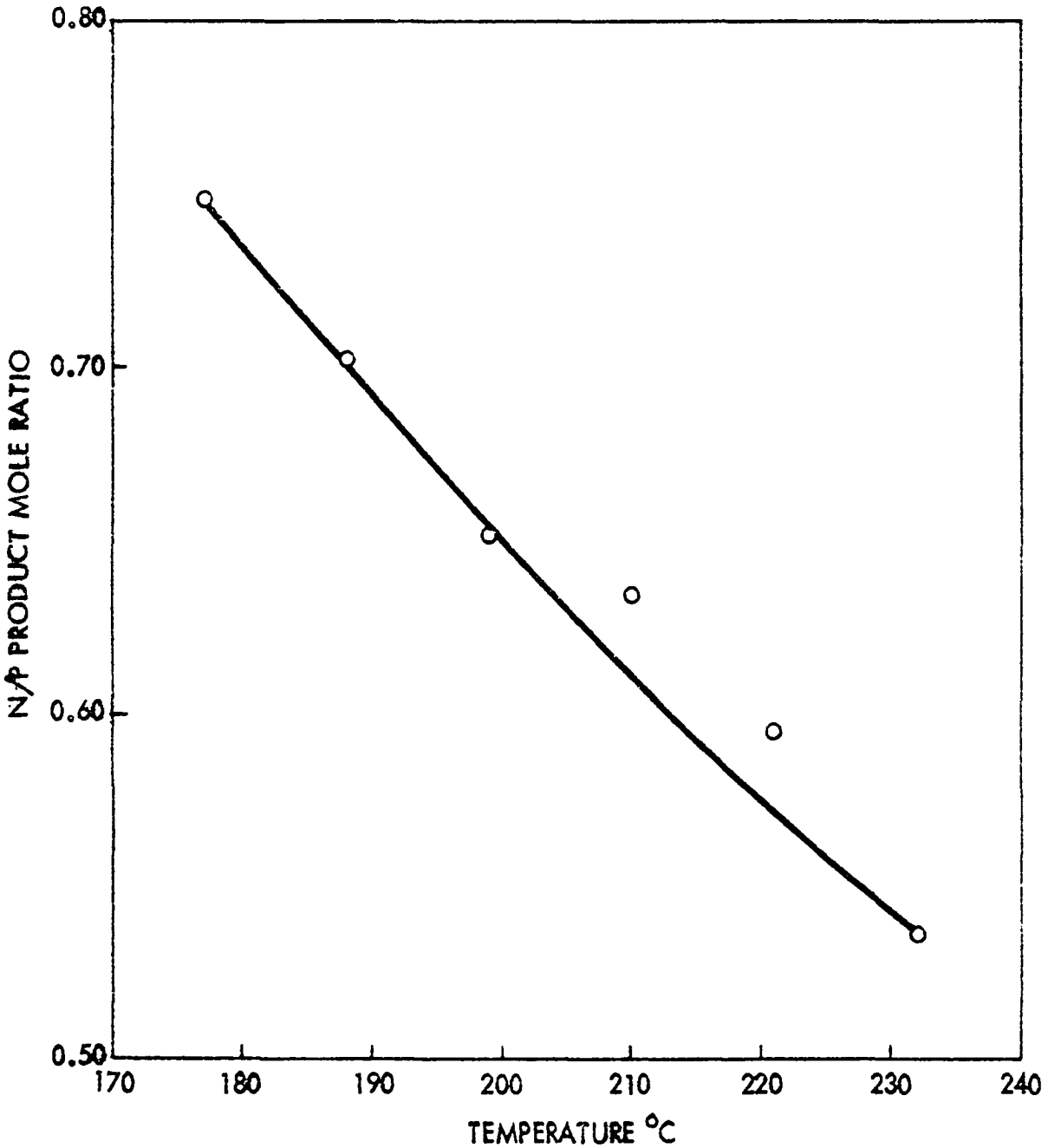
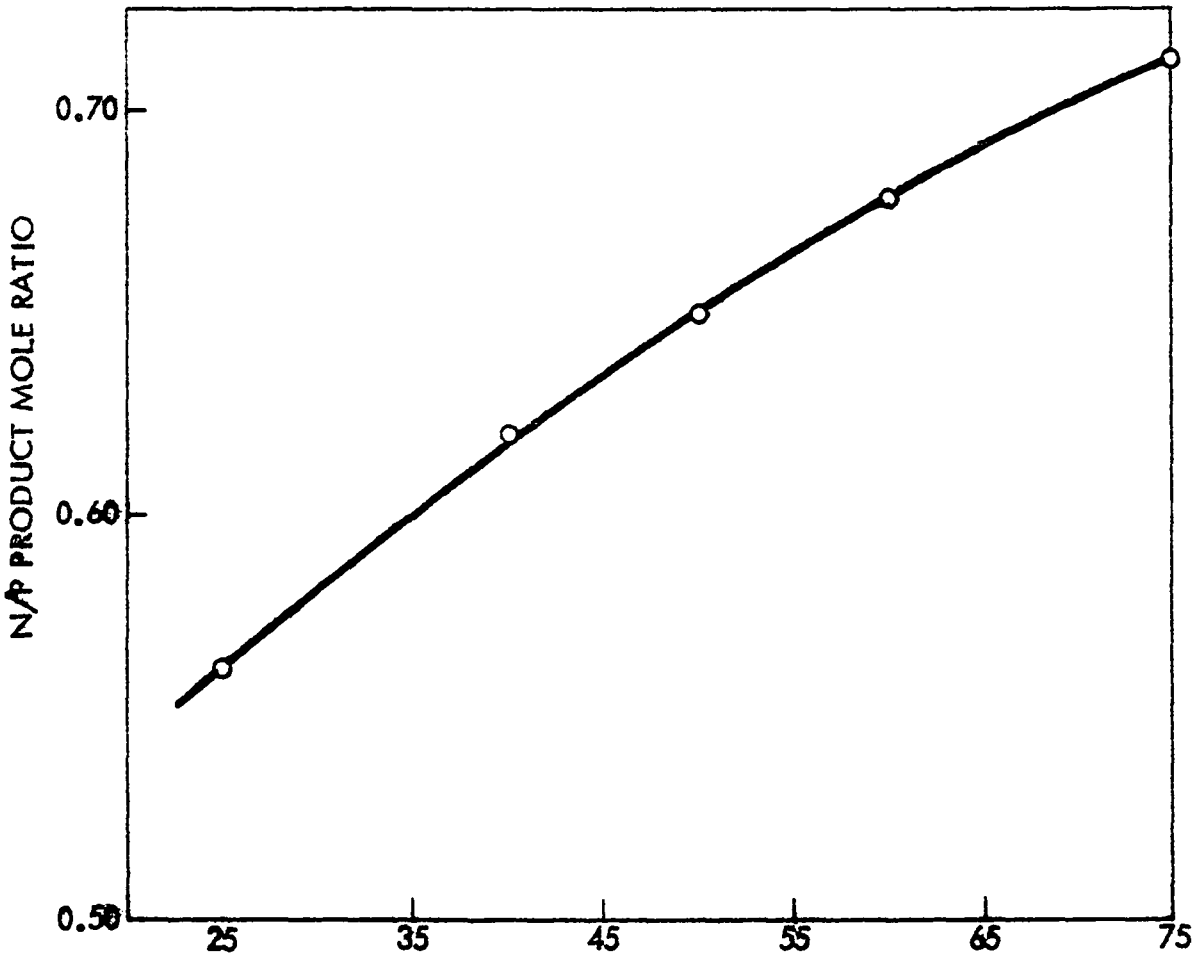
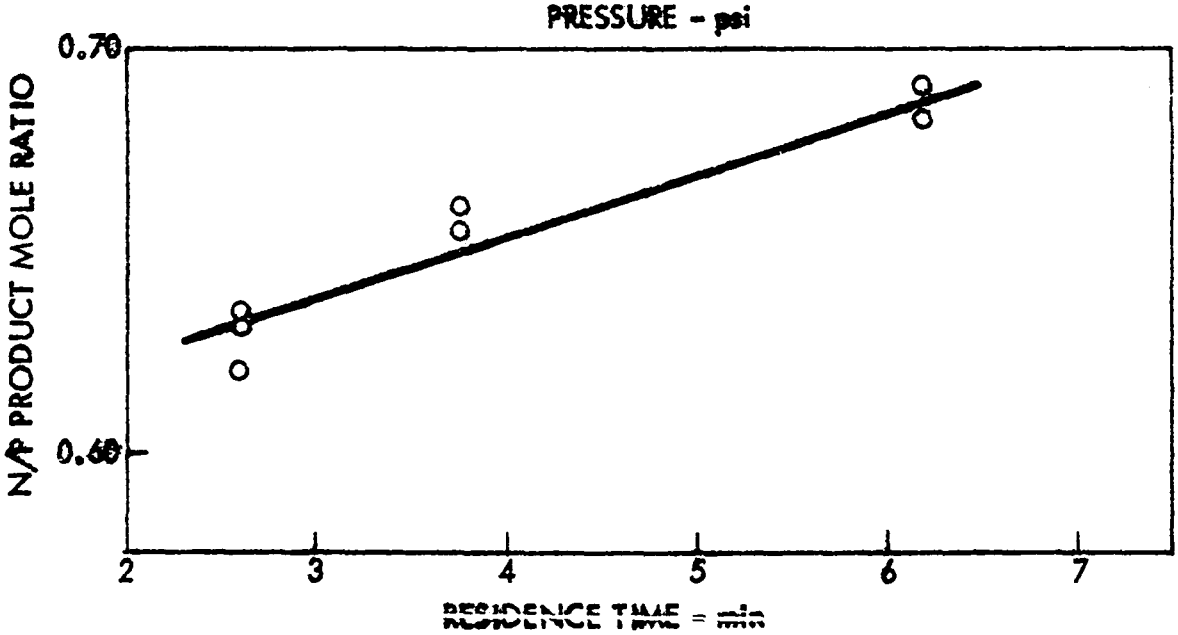

0.80
0.70
0.60
0.50
N/P PRODUCT MOLE RATIO
170
180
190
200
210
220
230
240
TEMPERATURE °C

Figure 22. Degree of ammoniation of product as a function of pressure - N/P product mole ratio versus pressure

Figure 23. Degree of ammoniation of product as a function of residence time - N/P product mole ratio versus residence time


0.70
0.60
0.50
N/P PRODUCT MOLE RATIO
25
35
45
55
65
75
PRESSURE - psi


0.70
0.60
N/P PRODUCT MOLE RATIO
2
3
4
5
6
7
RESIDENCE TIME = min

input actually reacted in the mixing tee and ammoniator reactor at this N/P feed ratio. However, when compared with the maximum degree of ammoniation obtained (N/P mole ratio of 0.748), it appears that an excess of ammonia was being used at this rate. No theoretical maximum degree of ammoniation can be determined, since this would vary with the proportions of ortho, pyro, and polyphosphates in the product. The maximum ammonia efficiency (95 %) was obtained at a N/P feed ratio of 0.25. This ammonia feed rate, however, was well below that required to obtain a product with at least five percent nitrogen. The low ammoniation efficiency in general was expected since no pre-ammoniation step was utilized as in the TVA ammonium polyphosphate process. In this step steam and unreacted ammonia would be passed through a prereactor where the ammonia would react with the incoming H_3PO_4-KH_2PO_4 feed. This partially ammoniated feed would then be pumped at a constant rate to be further ammoniated in the mixing tee and ammoniator reactor.

Based on the results of varying the N/P feed mole ratio the proper degree of ammoniation should be attained with a N/P feed mole ratio of 0.60 to 0.90 with a K/P feed mole ratio of 0.50 and an ammoniation efficiency of 95% or higher.

The effect of temperature was found to be one of the most important process variables as it affects the degree

of ammoniation of the product melt. As shown in Figure 21, when an excess of ammonia was fed at a constant rate while temperature of the reactor varied, the degree of ammoniation achieved decreased with increasing temperature. In the temperature range of 177 to 200°C great difficulty was encountered in keeping the product fluid. As the operating temperature in the ammoniator decreased, the degree of ammoniation likewise had to decrease in order to prevent freezing of the melt in the product lines. The product samples at 177°C actually had to be taken from the inside of the ammoniator reactor after the product had unavoidably frozen inside. In the temperature range of 200 to 232°C no problem of freezing occurred during the process. However, the degree of ammoniation decreased significantly in the higher temperature range.

The optimum operating temperature range for the ammoniator reactor melt must therefore be based on minimizing the ammonia loss due to high temperature and yet maintaining a fluid product in the reactor and product lines. This temperature range was 200 to 210°C when using a 0.50 mole ratio of K/P in the feed melt.

Pressure measurements in the reactor during ammoniation ranged up to seventy-five psi. In this range pressure was a significant variable affecting the degree of ammoniation of the product. Figure 22 shows that the degree of ammoniation

of the product increased from a N/P mole ratio of 0.562 at 25 psi to 0.712 at 75 psi. Pressure was the variable most difficult to maintain at a constant level. A differential pressure cell could be better used to feed ammonia into the ammoniator reactor. This would replace the ammonia rotameter and not only control the ammonia flow rate but also control the pressure in the ammoniator reactor more accurately.

Residence time had the least effect of all the process variables upon the degree of ammoniation of the product. This is shown in Figure 23. The ammoniation of the product ranged from a N/P mole ratio of 0.631 at 2.61 minutes residence time to 0.690 at 6.18 minutes. Although the residence time affected the ammoniation rate very little, it is very significant in determining the proportion of phosphorus that is in the polyphosphate form in the product. Also, the residence time affects the proportion of citrate insoluble phosphorus in the product. However, this was not encountered since reagent grade feed materials were used. This would definitely be a factor to consider if wet process phosphoric acid were one of the raw materials.

CONCLUSIONS

In the determination of the kinetic rate expression for the reaction between phosphoric acid and potassium chloride only the forward reaction portion was determined. It was concluded that the reaction rate was first order with respect to both chloride concentration and phosphoric acid concentration. The constants in the Arrhenius equation were determined for the forward portion of the reaction and are shown below.

$$\frac{-dC_{Cl}}{d\theta} = \left(2.72 \times 10^{6} \frac{\text{l.min.}}{\text{gm.mole.}}\right)\left(e^{\frac{-18{,}088 \text{ cal./gm.mole}}{RT}}\right) \times$$

$$(C_{Cl})(C_{H_3PO_4})$$

The experimental conditions under which these results were obtained can be found in Appendix C.

The ammoniation of a KH_2PO_4-H_3PO_4 melt can be successfully accomplished with the proper residence time, pressure, and temperature conditions. Using a K/P mole ratio of 0.50 in the feed melt the best operating conditions were found to be 200° to 210° C, with a pressure in excess of 40 psi, and a residence time above four minutes. Based on the experimental results, it was concluded that the degree of ammoniation of the final product increased with increasing pressure, increasing residence time, and decreasing temperature. The degree of neutralization ranged from a mole ratio of $(NH_4+K)/P$ of 0.737 to 1.238. Since no preammoniation step was used in

this process, this range is lower than that of TVA for ammoniation of super phosphoric acid into ammonium polyphosphate (up to 1.57 moles of N per mole of P).

As a result of the work with the experimental ammoniator reactor, it was concluded that the ammoniation portion of the NH_4-K-polyphosphate process can be carried out in the same processing equipment as used in the ammonium polyphosphate process. The most significant differences would be the need for higher temperatures and materials of construction that would be resistant to the additional corrosiveness of the chloride ion.

The theoretical heat of reactions calculated for many of the reactions both in the KCl-H_3PO_4 reaction process and in the ammoniation process are shown in Appendix A. These results would be of value in calculating heat inputs, cooling requirements and an overall heat balance for the process.

An empirical formula that represents the experimental product in chemical analysis was found to be $(NH_4)_{1.4}KH_{1.6}P_2O_7$. Proposed possible mixed salt formulas for the ammonium potassium polyphosphate components are also shown in Appendix A.

RECOMMENDATIONS

Based on the results and experience gained in working with the $KCl-H_3PO_4$ kinetics experiments several recommendations can be made. In purging the reaction system of HCl gas it would be much more desirable to use steam rather than heated air as used in the experimental work. It is recommended that the $KCl-H_3PO_4$ reaction take place at a temperature no lower than 160°C due to the higher residence times required for the KCl to be reacted below this temperature. However, increasing the reaction temperature above 200°C would severely dehydrate the reaction solution which really isn't necessary in this process.

Several improvements in the experimental equipment can be made. The ammoniator reactor was operated at the lower portion of its flow rate range. The feed input of the $KH_2PO_4-H_3PO_4$ could be increased and improved by replacing the present diaphragm pump with a larger capacity high pressure metering pump. Pressure control of the ammoniator reactor could be improved by controlling the ammonia input by means of a differential pressure cell. This would also eliminate the need for the ammonia rotameter used in measuring the ammonia flow rate.

The method of collecting ammonium potassium polyphosphate in a measured amount of distilled water involved

the possibility of error in the sample weight due to the loss of water as steam during the collection of the hot molten product. An alternate method of collecting the molten product would be to let it flow into a pan cooled by dry ice. This would freeze it quickly with a minimum of ammonia loss. Also the error in sample weight would not be involved in this method.

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ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. D. R. Boylan for his counsel and helpful suggestions and to the Engineering Research Institute for financial support. Thanks are also due to the fellow graduate students of the Chemical Engineering Department who contributed advice and equipment to the project knowingly or otherwise.

Also, the author wishes to express his gratitude to his wife Linda for her moral and other support during the past two years.

APPENDIX A

Thermodynamic Calculations

The theoretical enthalpy changes at standard conditions were calculated for the following reactions as shown below.

KCl aq. + H_3PO_4 aq. → KH_2PO_4 aq. + HCl g. + 16.82 kcal

$2KH_2PO_4$ aq. → $K_2H_2P_2O_7$ aq. + H_2O g. + 15.84 kcal

$K_2H_2P_2O_7$ aq. → $2KPO_3$ aq. + H_2O g. + 12.21 kcal

H_3PO_4 aq. + NH_3 g. → $NH_4H_2PO_4$ aq. - 21.96 kcal

NH_3 l. - 17.06 kcal

H_3PO_4 aq. + $2NH_3$ g. → $(NH_4)_2HPO_4$ aq. - 39.93 kcal

$2NH_3$ l. - 30.13 kcal

$2NH_4H_2PO_4$ aq. → $(NH_4)_2H_2P_2O_7$ aq. + H_2O g. + 16.66 kcal

$NH_4H_2PO_4$ aq. + $(NH_4)_2HPO_4$ → $(NH_4)_3HP_2O_7$ aq. + H_2O g. + 13.86 kcal

KH_2PO_4 aq. + NH_3 g. → KNH_4HPO_4 aq. - 21.34 kcal

NH_3 l. - 16.44 kcal

The following values of the standard heat of formation at 25°C were used in calculating the above heat of reaction values.

Table 2. Thermodynamic heat of formation values

Compound	$-\Delta H_f$ at 25°C kcal/gm mole[a]
NH_3 gas	10.944
NH_3 liquid	15.842
NH_4^+ aqueous	31.709
H_2O gas	57.842
HCl gas	22.038
H_3PO_4 aqueous	306.167
$NH_4H_2PO_4$ aqueous	339.070
$(NH_4)_2HPO_4$ aqueous	367.983
$HPO_4^=$ aqueous	307.529
$P_2O_7^{-4}$ aqueous	536.682
PO_3^- aqueous	235.127
$H_2P_2O_7^=$ aqueous	540.266
K^+ aqueous	60.311
KCl aqueous	99.881
KH_2PO_4 aqueous	367.266
K_2HPO_4 aqueous	426.048

[a]Calculated using the figures of Perry (16).

A sample calculation is shown below for the first equation.

$$KCl\ aq. + H_3PO_4\ aq. \rightarrow KH_2PO_4\ aq. + HCl\ g.$$

$$\Delta H = (\Delta H^\circ_f\ KH_2PO_4\ aq. + \Delta H^\circ_f\ HCl\ g.)$$

$$- (\Delta H^\circ_f\ KCl\ aq. + \Delta H^\circ_f\ H_3PO_4\ aq.)$$

= (-367.266 -22.038) - (-99.881 -306.167)

= + 16.820 kcal

Possible mixed salt formulas of ammonium potassium polyphosphate components are shown below.

NH_4KHPO_4

$(NH_4)_2KPO_4$

$NH_4K_2PO_4$

$NH_4KH_2P_2O_7$

$(NH_4)_2KHP_2O_7$

$(NH_4)_3KP_2O_7$

$NH_4K_2HP_2O_7$

$NH_4K_3P_2O_7$

$(NH_4)_a(K)_b(H)_cP_3O_{10}$ where (a+b+c)=5

APPENDIX B

Experimental Design Results

The results of the 2^4 factorial experimental design were calculated and are shown below for the H_3PO_4-KCl reactor.

Table 3. Statistical experimental design conditions

Factor	Factor Level	
A-Temperature	a_0-110°C,	a_1-140°C
B-Retention Time	b_0-10 min.,	b_1-30 min.
C-Aeration Rate	c_0-0 cc/min.,	c_1-500 cc/min.
D-H_3PO_4:KCl reactant mole ratio	d_0-1.33,	d_1-2.00

The F ratio indicates the degree of confidence that the individual factors are significant in affecting the percent reaction completeness.

Table 4. Factor F ratio results

Treatment	F ratio
A	43.26
B	27.61
C	8.37
D	3.92
AB	0.87

Table 4 (Continued)

Treatment	F ratio
AC	12.51
AD	0.05
BC	0.22
BD	1.62
CD	2.19
ABC	1.44
ACD	0.22
BCD	0.40
ABD	2.71
ABCD	1.60

The critical value of F at the 95% confidence level is $F_{1,15,a=0.05}$ equal to 4.54; therefore, one can accept factors A, B, AC, and C in that order as significantly affecting the degree of reaction completeness under the experimental conditions used. It should be noted that each of the aforesaid significant variables and the interaction influenced the percent reaction completeness in a positive manner.

APPENDIX C

$KCl-H_3PO_4$ Reaction Kinetics Data

Sample Number	θ - Minutes	C_{Cl} (gm moles/liter)	$C_{H_3PO_4}$ (gm moles/liter)	Temp °C
38-300-26-				
3	0	0.853	4.25	120
4	2	0.846		
5	4	0.827		
6	10	0.789		
7	20	0.748		
8	30	0.726		
9	0	0.460	4.50	120
10	2	0.456		
11	4	0.446		
12	10	0.414		
13	20	0.405		
14	0	0.233	4.66	120
15	2	0.231		
16	4	0.224		
17	10	0.229		
18	20	0.226		
19	0	1.21	4.02	120
20	2	1.19		
21	4	1.16		
22	10	1.11		
23	20	1.01		
40	0	0.460	4.50	140
41	2	0.447		
42	4	0.415		
43	10	0.367		
44	20	0.318		
45	30	0.258		
46	0	0.233	4.66	140
47	2	0.231		
48	4	0.208		
49	10	0.187		

Sample Number	θ - Minutes	C_{Cl} (gm moles/liter)	$C_{H_3PO_4}$ (gm moles/liter)	Temp °C
50	20	0.124		
51	30	0.069		
52	0	1.210	4.02	140
53	2	1.200		
54	4	1.070		
55	10	0.923		
56	20	0.755		
57	30	0.594		
38-300-32-				
3	0	1.000	4.18	100
4	2	1.006		
5	4	0.970		
6	10	0.956		
7	20	0.949		
8	30	0.870		
9	0	1.000	4.18	160
10	2	0.894		
11	4	0.674		
12	10	0.444		
13	20	0.309		
14	30	0.185		

Sample Number	θ - Minutes	C_{Cl_0}	ΔC_{Cl}	$C_{H_3PO_4}$	Temp °C
		(gm moles/liter)			
38-300-35-					
0	0	6.51	0	0.651	140
1	1		0.013	0.638	
2	2		0.043	0.608	
3	3		0.060	0.591	
4	4		0.084	0.567	
5	5		0.104	0.547	
6	6		0.126	0.525	
7	7		0.147	0.504	
8	8		0.174	0.477	
9	9		0.186	0.465	
10	10		0.204	0.447	
11	11		0.209	0.442	
12	12		0.232	0.419	

Sample Number	θ - Minutes	C_{Cl_0}	ΔC_{Cl}	$C_{H_3PO_4}$	Temp °C
		(gm moles/liter)			
13	13		0.249	0.402	
14	14		0.268	0.383	
15	15		0.267	0.384	
16	16		0.284	0.367	
17	17		0.261	0.390	
18	18		0.291	0.360	
19	19		0.304	0.347	
20	20		0.309	0.342	
22	22		0.322	0.329	
24	24		0.338	0.313	
26	26		0.344	0.307	
28	28		0.353	0.298	
30	30		0.358	0.293	

Summary of results

Temperature °C	k (l. min./gm mole)	α
100	0.00067	-
120	0.00198	1.15
140	0.00537	1.01
160	0.01657	-

$k_0 = 2.717 \times 10^6$ l.min./gm mole (using data from Figure 14)

E = 18,088 cal/gm mole (using data from Figure 15)

APPENDIX D

KH_2PO_4-H_3PO_4 Ammoniation Data

Table 5. KH_2PO_4-H_3PO_4 ammoniation data

Sample No.	N/P Feed Ratio (mole ratio)	%N Reacted	Temperature °C	Pressure psi
38-300-97-				
15	0.25	95	210	40
16	0.50	90	210	40
17	0.75	79	210	40
18	1.00	61	210	40
19	1.25	55	210	40
20	1.50	48	210	40
21	2.00	37	210	40
22	1.00	-	177	40
23	1.00	-	188	40
24	1.00	-	199	40
25	1.00	-	210	40
26	1.00	-	221	40
27	1.00	-	232	40
15-B	1.00	-	210	25
16-B	1.00	-	210	40
17-B	1.00	-	210	50
18-B	1.00	-	210	60
19-B	1.00	-	210	75
20-B	1.00	-	210	50
21-B	1.00	-	210	40
22-B	1.00	-	210	40
23-B	1.00	-	210	40
24-B	1.00	-	210	40

Residence Time - min.	N/P Ratio of Product (mole ratio)	% N	% P_2O_5	% K_2O
2.61	0.237	2.79	59.8	19.95
2.61	0.450	5.30	59.7	19.81
2.61	0.592	7.02	60.1	19.89
2.61	0.614	7.14	59.0	19.12
2.61	0.686	8.14	60.2	19.86
2.61	0.726	8.48	59.2	19.88
2.61	0.738	8.67	59.6	19.37
2.61	0.748	8.29	56.2	18.77
2.61	0.702	8.05	58.1	19.00
2.61	0.651	7.70	60.0	20.08
2.61	0.634	7.50	60.0	20.19
2.61	0.595	7.19	61.3	20.45
2.61	0.536	6.63	62.7	20.78
2.61	0.562	6.66	60.1	19.62
2.61	0.620	7.46	61.0	20.04
2.61	0.649	7.72	60.3	20.08
2.61	0.678	8.12	60.7	20.24
2.61	0.712	8.39	60.2	19.75
2.61	0.631	7.50	60.3	19.67
3.71	0.661	7.86	60.3	19.88
3.71	0.654	7.59	59.1	19.48
6.18	0.682	8.22	61.1	20.00
6.18	0.682	8.31	61.2	20.24